THEORETICAL DESCRIPTION OF POLARIZABILITIES
AND HYPERPOLARIZABILITIES USING COUPLED-CLUSTER METHODS

By

PIOTR B. ROZYCZKO

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1998

To my wife Ewa and our daughter Ola.

ACKNOWLEDGMENTS

I would like to thank Dr. Rodney J. Bartlett, whose dedication and persistency to teach quantum theory are limitless. His patience and open-mindedness have made the time I have spent working for him very enjoyable and interesting.

Thanks go to Dr. Yngve Öhrn for his excellent lectures on the subject of polarizator propagator, which were a very strong influence on the focus of my studies.

I would also like to express my acknowledgements to Dr. Henk Monkhorst, who was always very helpful to me and never left my questions unanswered.

Thanks go to Dr. Mike Zerner for assuring me that writing a thesis is not as hard or as scary as I thought.

I would like to thank Dr. Jim Deyrup, who helped me enormously right after my arrival to this University and throughout my entire studies.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

THEORETICAL DESCRIPTION OF POLARIZABILITIES
AND HYPERPOLARIZABILITIES USING COUPLED-CLUSTER METHODS

By

Piotr B. Rozyczko

December 1998

Chairman: Dr. Rodney J. Bartlett
Major Department: Chemistry

This thesis is devoted to the development and application of new theoretical methods based on the coupled cluster formalism designed for better and more general description of linear and nonlinear electro-optic effects in molecules.

Starting with the general perturbation theory we derive equations for linear polarizability and first- and second-order hyperpolarizability. We present both the derivation and numerical results for the analytic Equation of Motion Coupled Cluster (EOM-CC) method, the BW-EOM-CC (Brillouin-Wigner EOM-CC) method and the less attractive but more numerically complete energy derivative formula.

We describe in detail the advantages and disadvantages of including the renormalization terms in the Sum Over States (SOS) expression, widely used for this type of calculations, show ways to eliminate some of these terms and discuss their numerical importance.

Our most powerful method BW-EOM-CC based on the Brillouin-Wigner perturbation expansion is attractive for many reasons. It not only is fully size-extensive but also permits calculations of the properties at the frequency of electron resonance, where all other methods based on the Rayleigh-Schrödinger perturbation theory fail.

We report the numerical results for several interesting systems, including the *trans*-butadiene. Theoretical prediction of nonlinear properties of this molecule has become a true test of quality and accuracy of any new method.

CHAPTER 1
INTRODUCTION

Nonlinear optics is the knowledge about phenomena occurring as a consequence of the modification of the optical properties of a chemical system by the presence of light. Such phenomena are considered nonlinear because they take place when the response of a system depends in a nonlinear (quadratic, cubic, quartic, etc.) manner upon the strength of the electric field.

In 1961 Franken, Hill, Peters and Weinreich [1] demonstrated the first nonlinear optical effect, in which ultraviolet radiation at the second harmonic of the ruby laser (3471Å) was observed when a ruby laser beam at 6942Å was focused on a quartz crystal. Franken's experiment confirmed the existence of the nonlinear effects and showed that with the optical field strengths available from lasers, effects due to the second harmonic generation could become significant. It takes a field of a strength of approximately 1kV/cm to induce a nonlinear response in a system and no conventional source of light can deliver this intensity. Thus, although harmonic generation of electromagnetic waves had been known for a long time, physicists needed the power of laser to explore the nonlinear world. Almost at the same time, Kaiser and Garrett [2] observed another nonlinear effect produced by a laser beam. It was a two-photon absorption giving rise to the second order hyperpolarizability . Since then, numerous nonlinear optical phenomena have been discovered. They have not only greatly enhanced our knowledge about interaction of light and matter, but also created a revolution in optical technology. Nonlinear optical properties offer one of the most challenging frontiers for modern quantum chemical studies. Highly nonlinear materials are being used in many optical devices like lasers, optical switches and modulators. There are two aspects of a

1

practical interest in nonlinear optics: The most important of these is frequency conversion, in which laser radiation at one frequency is converted, for example by harmonic generation or sum-frequency generation, into coherent radiation at a new frequency. Because the converted radiation may be at a frequency that is not readily available from a laser source, these frequency-conversion techniques provide an important means of extending the spectral range of lasers. Converting high-energy light from an infrared laser to the visible frequencies would greatly increase the density of recorded information on optical media such as CD-ROMs. Another aspect is in telecommunication transmission, where information is sent on a low energy carrier by placing a *dc* electric field across the material. This gave rise to an extremely fascinating area of optical quantum computing.

These practical aspects are governed by the interaction of electromagnetic radiation with matter.

Optical properties can be expressed in terms of microscopic quantities: polarizabilities and hyperpolarizabilities, which are amenable to quantum chemical evaluation. The Hartree-Fock based methods have been known and used for a long time (TDHF [3, 4, 5] also known as RPA [6]), but their accuracy is not sufficient to be predictive for engineers and chemists. In order to describe hyperpolarizabilities more reliably, it is necessary to use sufficiently big basis sets, to introduce electron correlation effect, frequency dependence and vibrational corrections. Basis sets need the flexibility to describe any polarization of the electronic cloud induced by an external electric field, correctly. The effect of electron correlation increases with the order of a property; for linear polarizabilities it rarely exceeds 15%, whereas, the correlation correction for β in the case of ammonia reaches 70% of the total value [7].

A very important factor is the frequency dependence. The experimental data always refer to dynamical processes and therefore relate to frequency dependent

properties. The extrapolation to zero frequency often introduces problems for the comparison between theory and experiment.

Vibrational corrections can constitute as much as 10% of the total value of a given dynamical property; therefore, some effort is also addressed at including that correction [8].

Most of the limitations for the electronic problem can be overcome by employing correlated methods, together with large basis sets containing polarization and diffuse functions. So far, there are very few applications of frequency-dependent correlated methods for hyperpolarizabilities: Multi-Configurational Linear Response theory (MCLR) [9, 10] and Multi-Configurational Time-Dependent Hartree-Fock method (MCTDHF) [11, 12]. Two groups; Rice and Handy [13, 14] and Aiga, Sasagane and Itoh [15, 16] derived the formulas for frequency-dependent second-order perturbation theory method MBPT(2). For the first hyperpolarizability, the last group also extended their quasienergy derivative method for the Brueckner coupled-cluster case [17]. Another approach to this problem is the equation of motion (EOM) theory [18, 19, 20]. It has been successfully applied to dynamical polarizability calculations [21], and to the hyperpolarizabilities that occur in the Kerr effect by combining analytically computed dynamic polarizabilities with finite-field differentiation.

CHAPTER 2
MOLECULAR STATIC AND DYNAMIC PROPERTIES

2.1 Introduction

The energy of a molecule in an external electric field can be expressed as a power series:

$$E(\hat{\varepsilon}) = E(0) - \sum_i \mu_i \varepsilon_i - \frac{1}{2!} \sum_{ij} \alpha_{ij} \varepsilon_i \varepsilon_j \quad - \quad \frac{1}{3!} \sum_{ijk} \beta_{ijk} \varepsilon_i \varepsilon_j \varepsilon_k -$$
$$\frac{1}{4!} \sum_{ijkl} \gamma_{ijkl} \varepsilon_i \varepsilon_j \varepsilon_k \varepsilon_l - ... \quad (2.1)$$

where ε_x is the field strength in x direction, etc. and μ, α, β, γ,... are coefficients of the expansion. These coefficients are physical, measureable quantities; dipole moment, polarizability, and first and higher hyperpolarizabilities.

The above equation can be rewritten in terms of the induced dipole moment [22] , as the first derivative of the total energy with respect to the external field strength $\hat{\varepsilon}$:

$$-\left(\frac{\partial E(\varepsilon)}{\partial \varepsilon_i}\right) = \mu_i + \sum_j \alpha_{ij} \varepsilon_j + \frac{1}{2!} \sum_{jk} \beta_{ijk} \varepsilon_j \varepsilon_k + \frac{1}{3!} \sum_{jkl} \gamma_{ijkl} \varepsilon_j \varepsilon_k \varepsilon_l + ... \quad (2.2)$$

Using this expression we can define the polarizability α as a first-order, linear (in external field strength) response property of a molecule in an electric field. The first hyperpolarizability β is then defined as a second-order, nonlinear property, γ as a third order property, etc.

There are two general ways to define molecular properties;

1 - Energy derivatives, and

2 - Perturbation expansion.

The energy derivative method also can be divided in two classes:

5

- Finite field, numerical differentiation, and

- Analytical derivatives.

Below we will summarize these methods, paying particular attention to their importance in the evaluation of higher-order nonlinear properties.

Finite field derivatives

Differentiating Eq. (2.1) with respect to the external field strength, and evaluating the derivative at the limit $\varepsilon_j, \varepsilon_k, \varepsilon_l, \varepsilon_m, ... \to 0$, we obtain the expression for a linear polarizability:

$$\alpha_{ij} = -\left(\frac{\partial^2 E(\hat{\varepsilon})}{\partial \varepsilon_i \partial \varepsilon_j}\right).\tag{2.3}$$

Similarly for hyperpolarizabilities we get

$$\beta_{ijk} = -\left(\frac{\partial^3 E(\hat{\varepsilon})}{\partial \varepsilon_i \partial \varepsilon_j \partial \varepsilon_k}\right),\tag{2.4}$$

$$\gamma_{ijkl} = -\left(\frac{\partial^4 E(\hat{\varepsilon})}{\partial \varepsilon_i \partial \varepsilon_j \partial \varepsilon_k \partial \varepsilon_l}\right),\tag{2.5}$$

and so on.

Using a simple mathematical formulas for numerical differentiation and approximating infinitely small increments of the electric field by finite values we can obtain the finite electric field derivative formulas. The dipole moment will be then expressed as the finite first-order derivative of the energy with respect to the external field strength:

$$\mu(i) = \frac{E_i(\epsilon_1) - E_i(\epsilon_2)}{\epsilon_2 - \epsilon_1}\tag{2.6}$$

The best simple method for evaluating numerical derivatives is a central difference formula where $\epsilon_1 = \epsilon$ and $\epsilon_2 = -\epsilon$. This gives

$$\mu_i = \frac{E_i(\epsilon_i) - E_i(-\epsilon_i)}{2\epsilon_i}\tag{2.7}$$

Applying the above formula to the linear and nonlinear polarizabilities we obtain

$$\alpha_{ij} = \frac{\mu_i(\epsilon_j) - \mu_i(-\epsilon_j)}{2\epsilon_j} = \frac{E_i(2\epsilon_j) + E_i(-2\epsilon_j) - 2E_i(0)}{4\epsilon_j^2} \qquad (2.8)$$

$$\beta_{ijk} = \frac{\alpha_{ij}(\epsilon_k) - \alpha_{ij}(-\epsilon_k)}{2\epsilon_k} \qquad (2.9)$$

$$\gamma_{ijkl} = \frac{\beta_{ijk}(\epsilon_l) - \beta_{ijk}(-\epsilon_l)}{2\epsilon_l} \ . \qquad (2.10)$$

The numerical differences method is a very convenient method as it delivers values of the properties at any order at which the single point energy can be calculated. It can be thus extremely useful serving as a good benchmark and assuring accuracy of a new method.

Drawbacks of the finite field method are on the other hand numerous. First of all it is very expensive–a single tensor element of the second hyperpolarizability γ requires 5 separate calculations at different electric field strengths. Also, the choice of the field strength is a trade-off between the accuracy of the result (the smaller the field is, the closer to the full derivative the result is) and the magnitude of an effect (large field causes a bigger response and more significant digits in the answer). Also, it is very difficult if not impossible to calculate any frequency dependent properties, as it requires an analytical frequency dependent code for lower-order derivatives.

Derivatives as perturbative energy corrections

Let us define a perturbed Hamiltionian as

$$H(\varepsilon) = H_0 + \varepsilon V, \qquad (2.11)$$

where H_0 is the unperturbed Hamiltonian, and V is the perturbation. For the properties of interest, V is a electric dipole moment in x,y or z direction. The corresponding Schrödinger equation with ε-dependent wavefunction, Hamiltionian

and eigenenergy can be written as

$$H(\varepsilon)\psi(\varepsilon) = E(\varepsilon)\psi(\varepsilon). \tag{2.12}$$

Differentiating the resulting expectation value of $H(\varepsilon)$ with respect to the field strength, we get

$$E(\varepsilon)\langle\psi(\varepsilon)|\psi(\varepsilon)\rangle = \langle\psi(\varepsilon)|H(\varepsilon)|\psi(\varepsilon)\rangle, \tag{2.13}$$

$$\langle\psi(\varepsilon)|H(\varepsilon) - E(\varepsilon)|\frac{\partial\psi(\varepsilon)}{\partial\varepsilon}\rangle + \langle\frac{\partial\psi(\varepsilon)}{\partial\varepsilon}|H(\varepsilon) - E(\varepsilon)|\psi(\varepsilon)\rangle =$$
$$\langle\psi(\varepsilon)|\frac{\partial H(\varepsilon)}{\partial\varepsilon} - \frac{\partial E(\varepsilon)}{\partial\varepsilon}|\psi(\varepsilon)\rangle. \tag{2.14}$$

Two first terms of the above equation vanish, since as $\varepsilon \to 0$, $H(\varepsilon) \to H_0, E(\varepsilon) \to E_0$ and we have $(H_0 - E_0)|\psi_0\rangle = \langle\psi_0|(H_0 - E_0) = 0$. This leads to

$$\frac{\partial E(\varepsilon)}{\partial\varepsilon}|_{\varepsilon=0} = \langle\psi_0|\frac{\partial H(\varepsilon)}{\partial\varepsilon}|\psi_0\rangle|_{\varepsilon=0} = \langle\psi_0|V|\psi_0\rangle \equiv E_{RSPT}^{(1)}. \tag{2.15}$$

Taking the second derivative of the expectation value (2.14) gives (assuming the wavefunction to be real)

$$\frac{\partial^2 E(\varepsilon)}{\partial\varepsilon^2}|_{\varepsilon=0} = 2\langle\psi_0|\frac{\partial H(\varepsilon)}{\partial\varepsilon}|\frac{\partial\psi_0}{\partial\varepsilon}\rangle|_{\varepsilon=0} = 2\langle\psi_0|V|\psi^{(1)}\rangle \equiv 2E_{RSPT}^{(2)}. \tag{2.16}$$

And in general,

$$\frac{\partial^{(n)} E(\varepsilon)}{\partial\varepsilon^n} = \langle\psi_0|\frac{\partial H(\varepsilon)}{\partial\varepsilon}|\frac{\partial^{(n-1)}\psi_0}{\partial\varepsilon^{(n-1)}}\rangle = \langle\psi_0|V|\psi^{(n-1)}\rangle \equiv (n!)E_{RSPT}^{(n)}. \tag{2.17}$$

Hence the perturbation theory may be straightforwardly used in evaluation of molecular response properties, like (hyper)polarizabilities.

2.1.1 First Hyperpolarizability, β

The first polarizability β corresponds to a second-order, nonlinear process, and it can be categorized by frequency, intensity and phases of the field components.

The second-order nonlinear tensor element is expressed as

$$\beta_{ijk}(-\omega_3; \omega_1, \omega_2) \tag{2.18}$$

where $\omega_3 = \omega_1 \pm \omega_2$, and i,j,k are the Cartesian components of the interacting fields and polarization waves. In general, each component is associated with a frequency component in the argument of β. Assuming the Kleinmann symmetry [23], i.e. choosing the incident frequencies far from resonance, Cartesian indices and frequency components can be permuted together. There are two physical interpretations of β; in one of them, the field associated with the first beam with frequency ω_1 alters the refractive index of the medium and the propagation characteristics of the second beam with frequency ω_2 is modified accordingly, is phase modulated and exhibits sidebands at frequencies $\omega_1 + \omega_2$ and $\omega_1 - \omega_2$. If both incoming beams have the same frequency, a harmonic overtone at 2ω is created. The other interpretation describes the nonlinear effects as resulting from nonlinearities in the polarization response to incident fields at various frequencies. A medium is composed of a set of classical anharmonic oscillators, describing, physically, an electron bound to a core. Here, new frequency components of the polarization at $\omega_1 \pm \omega_2$, $2\omega_1$, $2\omega_2$ and 0 appear through quadratic interaction of the field with oscillators via the anharmonic terms.

In the case where $\omega_1 = \omega_2 = \omega$, we have one of the best known effects in nonlinear optics; second harmonic generation, SHG expressed as $\beta(-2\omega; \omega, \omega)$. In this process, the energy is redistributed between the fields as a result of interaction of the waves with the medium. To have efficient redistribution of energy, momentum must be conserved. This condition is known as phase matching. The implication here is that energy can only be transferred from the fundamental to the harmonic field, as the waves propagate through the medium, as long as they maintain the required phase relationship.

If $\omega_1 = 0$ and $-\omega_3 = \omega_2 = \omega$, we speak about an electrooptic effect (EOE), where a dc static field is applied to the medium, altering the refractive index, and, hence, the propagation characteristics rather than the frequency of light. This is written as

$$\beta_{ijk}(-\omega; 0, \omega) \tag{2.19}$$

The last second-order nonlinear effect is an optical rectification (OR),

$$\beta_{ijk}(0; -\omega, \omega) \tag{2.20}$$

for which $\omega_3 = 0$ and $\omega_1 = -\omega_2$. Here, two beams with frequency ω interact to produce a dc polarization of the medium. Assuming validity of the Kleinman symmetry [23], we have

$$\beta_{abc}(-\omega; 0, \omega) = \beta_{cab}(0; -\omega, \omega), \tag{2.21}$$

which shows that EOE and OR are closely related.

From Eq. (2.17) we note that to calculate β, one needs to know the second-order perturbed wavefunction. Recalling the RSPT formulas;

$$E^{(2k+1)} = \langle \psi^{(0)} | V | \psi^{(2k)} \rangle = \langle \psi^{(k)} | V - E^{(1)} | \psi^{(k)} \rangle, \tag{2.22}$$

where

$$|\psi^{(k)}\rangle = R_0 \left(V - E^{(1)} \right) |\psi^{(k-1)}\rangle - \sum_{l=2}^{k-1} E^{(l)} |\psi^{(k-l)}\rangle. \tag{2.23}$$

Here $|\psi^{(n)}\rangle$ is the n-th order wavefunction, V is an external perturbation potential, and R_0 is the resolvent operator;

$$R_0 = \sum_{i,j \neq 0} |\psi_i^{(0)}\rangle \langle \psi_i^{(0)} | E_0 - H_0 \pm \omega | \psi_j^{(0)}\rangle^{-1} \langle \psi_j^{(0)} | . \tag{2.24}$$

The first hyperpolarizability can be viewed as

$$\beta \equiv 6E^{(3)} = 6\langle\psi^{(0)}|V|\psi^{(2)}\rangle = 6\langle\psi^{(1)}|V - E^{(1)}|\psi^{(1)}\rangle. \tag{2.25}$$

Using Eq. (2.23) the above expression can be rewritten as

$$\beta_{ijk} = 6\langle\psi_0^{(0)}|V_a R_0 \left(V_b - \langle V_b\rangle\right) R_0 V_c|\psi_0^{(0)}\rangle . \tag{2.26}$$

The full expression for a specific tensor element of the second harmonic generation then becomes [24]

$$\begin{aligned}\beta_{ijk}(-2\omega;\omega,\omega) = \quad & F_{ijk}(-2\omega,-\omega) + F_{ijk}(2\omega,\omega) + F_{ikj}(-2\omega,-\omega) + \\ & F_{ikj}(2\omega,\omega) + F_{kij}(-2\omega,-\omega) + F_{kij}(2\omega,\omega) \end{aligned} \tag{2.27}$$

with the frequency dependent moment defined as

$$F_{ijk}(n\omega, m\omega) = \sum_{pq\neq 0} \frac{\langle\psi_0|V_i|\psi_p\rangle\langle\psi_p|V_j - \langle V_j\rangle|\psi_q\rangle\langle\psi_q|V_k|\psi_0\rangle}{(E_p + n\omega)(E_q + m\omega)} . \tag{2.28}$$

$\langle V_x\rangle$ being the expectation value of the perturbation, $\langle\psi_0|V_x|\psi_0\rangle$.

2.1.2   Second Hyperpolarizability, γ

In general, third-order nonlinear properties can be viewed as resulting from four-wave mixing. There are numerous third-order processes that can be distinguished on the basis of frequencies of the output and input beams. The most important case is a Third-Harmonic Generation (THG), where all three incoming waves have the same frequency ω, and the resulting response is a beam at the frequency 3ω;

$$\gamma_{ijkl}\left(-3\omega;\omega,\omega,\omega\right). \tag{2.29}$$

If one of the frequencies has a negative phase, we observe an effect called the Intensity-Dependent Refractive Index (IDRI), and the process is described by the

following expression:

$$\gamma_{ijkl}\left(-\omega; \omega, \omega, -\omega\right). \tag{2.30}$$

Incident frequencies do not necessarily have to be the same; an example is one of the most important third-order effects, called the Optical Kerr Effect (OKE):

$$\gamma_{ijkl}\left(-\omega_1; \omega_1, \omega_2, -\omega_2\right). \tag{2.31}$$

Introducing a static dc component of the incident field, we can observe 4 more processes: direct current-Induced SHG (dc-SHG), Electro-Optic Kerr Effect (EOKE) and direct current-Induced Optical Rectification (dc-OR).

From Eq. (2.17) we have

$$\gamma = 24E^{(4)} = 24\langle\psi^{(0)}|V|\psi^{(3)}\rangle \equiv 24\langle\psi^{(1)}|V - E^{(1)}|\psi^{(2)}\rangle \equiv 24\langle\psi^{(2)}|V - E^{(1)}|\psi^{(1)}\rangle.$$

$$\tag{2.32}$$

Inserting Eq. (2.23) into the above expression we obtain

$$\begin{aligned}
\gamma_{ijkl} &= 24\langle\psi^{(0)}|V_i R_0 \left(V_j - E_j^{(1)}\right) R_0 \left(V_k - E_k^{(1)}\right) R_0 V_l|\psi^{(0)}\rangle - \\
&\quad 24E^{(2)}\langle\psi^{(0)}|V_k R_0^2 V_l|\psi^{(0)}\rangle.
\end{aligned}$$

$$\tag{2.33}$$

The second term is a normalization part cancelling unlinked diagrams arising in the former term. If we include only linked terms in the above equation, we can leave the renormalization term out:

$$\gamma_{ijkl} = 24\langle\psi^{(0)}|V_i R_0 \left(V_j - E_j^{(1)}\right) R_0 \left(V_k - E_k^{(1)}\right) R_0 V_l|\psi^{(0)}\rangle_L. \tag{2.34}$$

2.2 Description Using Hartree-Fock Methods

Theoretical description of linear and nonlinear processes in molecules using analytical (not finite-field derivatives) methods began almost simultaneously with

the development of time dependent field wavefunction. The fully analytical formulation of the *ab initio* frequency dependent polarizability and hyperpolarizabilities dates back to 1986, when H. Sekino and R.J. Bartlett [3] derived and evaluated these properties using time dependent Hartree-Fock theory (TDHF). They utilized the recursiveness of the TDHF theory and developed formulas that were applicable to any order. This method also incorporates the $2n + 1$ rule for energy expression [25], stating that the $2n + 1$ energy order can be computed by using just the nth-order TDHF wavefunction, which can offer an additional simplification.

Starting from the Schrödinger equation in the time dependent formalism,

$$\mathbf{FC} - i\frac{\partial}{\partial t}\mathbf{SC} = \mathbf{SC}\epsilon \,, \tag{2.35}$$

and expanding the time dependent coefficient matrix $\mathbf{C}$ by orders with respect to the external oscillating perturbation and limiting the derivation to a single monochromatic and static fields Sekino and Bartlett obtained the final expressions in terms of density matrices:

$$\alpha(-\omega;\omega) = -Tr\left\{\mathbf{H}^{(1)}\mathbf{D}(\pm\omega)\right\} \,,$$

$$\beta(-2\omega;\omega,\omega) = -2Tr\left\{\mathbf{H}^{(1)}\mathbf{D}(\pm\omega,\pm\omega)\right\} \,,$$

$$\gamma(-3\omega;\omega,\omega,\omega,\omega) = -6Tr\left\{\mathbf{H}^{(1)}\mathbf{D}(\pm\omega,\pm\omega,\pm\omega)\right\} \, ... \tag{2.36}$$

$\mathbf{D}$ is the density matrix defined for first-order as

$$\mathbf{D}(\pm\omega) = \mathbf{C}(\pm\omega)\mathbf{n}\mathbf{C}^{(0)\dagger} + \mathbf{C}^{(0)}\mathbf{n}\mathbf{C}(\mp\omega)^{\dagger} \,, \tag{2.37}$$

and for the second-order as

$$\mathbf{D}(\pm\omega,\pm\omega) = \mathbf{C}(\pm\omega,\pm\omega)\mathbf{n}\mathbf{C}^{(0)\dagger} + \mathbf{C}(\pm\omega)\mathbf{n}\mathbf{C}(\mp\omega)^{\dagger} + \mathbf{C}^{(0)}\mathbf{n}\mathbf{C}(\mp\omega,\mp\omega)^{\dagger} \,. \tag{2.38}$$

In general, for any meaningful order n, the TDHF hyperpolarizability can be expressed in terms of the n-th derivative of the density matrix with respect to the

electric field strength $\mathbf{E}$:

$$
\begin{aligned}
\chi^{(n)}(-n\omega; \omega, ...) &= -Tr\left\{\mathbf{H}^{(1)}\frac{\partial^{(n)}}{\partial\mathbf{E}^{(n)}}\mathbf{D}\right\} \\
&= -n!Tr\left\{\mathbf{H}^{(1)}\mathbf{D}(\pm\omega, ...)\right\}.
\end{aligned}
$$

The static (time independent) formulation of the coupled-perturbed Hartree-Fock (CPHF) obeying the $2n+1$ rule had been implemented by Dykstra and Jasien [26] a few years earlier in 1984, but it is the frequency or time dependent processes that are of the highest importance in chemistry and physics. Thus we will concentrate on methods that include the frequency dependence.

Unfortunately, the accuracy of the TDHF based methods is not sufficient to be predictive for engineers and chemists. In order to describe hyperpolarizabilities more reliably, it is necessary to use sufficiently large basis sets and introduce electron correlation effect. Basis sets need the flexibility to describe any polarization of the electronic cloud induced by an external electric field, correctly. The effect of electron correlation increases with the order of a property; for linear polarizabilities it rarely exceeds 15%, whereas, the correlation correction for β in the case of ammonia reaches 70% of the total value [7].

2.3 Description Using Correlated Methods

2.3.1 Many-Body Perturbation Theory Based Methods

The first known correlated, single-reference, fully analytical treatment of frequency dependent hyperpolarizabilities dates back to 1991, when Rice and Handy [13] formulated and implemented the second-order Møller-Plesset perturbation theory expressions. To achieve their goal, the authors used a concept of pseudo-energy $W(t)$ defined to be the time-dependent eigenvalue of the operator $H - i[\partial(\partial t)]$.

$$
\left(\mathbf{H} - i\frac{\partial}{\partial t}\right)\Phi = \mathbf{W}(t)\Phi \tag{2.39}
$$

Here, solution of this equation is the same as solving the standard time-dependent Schrödinger equation

$$\mathbf{H}\Psi = i\left(\frac{\partial}{\partial t}\right)\Psi \ .$$

(2.40)

where

$$\Psi = \Phi exp\left(-i\int \mathbf{W}(t)dt\right).$$

(2.41)

$W(t)$ was then expanded in a power series in $E(\omega) = E(0) + 1/2E(\omega)\left(e^{i\omega t} + e^{-i\omega t}\right)$, with $W(0)$ being the static eigenvalue. The partitioning of the Hamiltonian is then applied, where the unperturbed part is the time independent Hamiltonian H_0 and the perturbation H' is defined as $-i[\partial/(\partial t)]$.

$$H_0 = F - i\frac{\partial}{\partial t}$$

(2.42)

$$H' = H - F$$

(2.43)

where

$$F = F_0 - i\frac{\partial}{\partial t}$$

(2.44)

From here, the first derivative of the quasi-energy W with respect to the external field strength (time-dependent dipole moment), second derivative (polarizability) and third derivative (first hyperpolarizability β is evaluated as a complicated and not recursive expression [13, 14]) as *corrections* to the unperturbed (static) values:

$$\alpha_{ij}(-\omega;\omega)\cos(\omega t) = \alpha_{ij}(0;0)\cos(\omega t) + i\frac{\partial}{\partial E_i}\frac{\partial}{\partial t}\langle\Psi|\frac{\partial\Psi}{\partial E_{\omega j}}\rangle \ ,$$

(2.45)

$$\beta_{ijk}(-\omega;0,\omega)\cos(\omega t) = \beta_{ijk}(0;0,0)\cos(\omega t) + \frac{\partial^2}{\partial E_i\partial E_j}\frac{\partial}{\partial t}\langle\Psi|\frac{\partial\Psi}{\partial E_{\omega k}}\rangle \ .$$

(2.46)

The numerical results presented by Rice and Handy on ammonia and formaldehyde prove that it is desirable to determine the frequency dependent contribution to the (hyper)polarizability at the correlated rather than SCF level, especially in

cases, where the frequency dependent contribution is significant, such as the SHG process.

2.3.2 Linear and Quadratic Response Methods

Another way to describe the linear and nonlinear properties is the response function [27], or propagator formalism [28, 29]. The response method can be applied to any wavefunction, and therefore there have been many different formulations of the method. Response theory methods for calculations of molecular properties have recently been vastly improved. These methods are based on both non-correlated SCF and correlated and multi-configurational SCF (MCSCF) reference wave functions.

The response functions are defined by considering the expansion coefficients of the expectation value of a (time-independent) perturbation operator. In case of optical properties of interest, this operator is the dipole moment operator μ [30].

$$
\mu_r(t) = \langle \Psi(t)|\mu|\Psi(t)\rangle = \langle \Psi|\mu|\Psi\rangle + \int \langle\langle \mu; V(\omega_1)\rangle\rangle_{\omega_1} \exp(-i\omega_1 t)d\omega_1
$$
$$
+1/2 \int \int \langle\langle \mu; V(\omega_1); V(\omega_2)\rangle\rangle_{\omega_1,\omega_2} \exp(-i\omega_1 - i\omega_2)t d\omega_1 d\omega_2
$$
$$
+1/6 \int \int \int \langle\langle \mu; V(\omega_1); V(\omega_2); V(\omega_3)\rangle\rangle_{\omega_1,\omega_2,\omega_3} \exp(-i\omega_1 - i\omega_2 - i\omega_3)t d\omega_1 d\omega_2 d\omega_3 \ .
$$

$$(2.47)$$

Comparing Eqns. (2.2) and (2.47) one can readily see that the response functions $\langle\langle \mu; V(\omega)...\rangle\rangle$ define the properties of interest. The first, linear response function defines polarizability α and can be evaluated as a Sum-Over-States expression [30]:

$$
\alpha_{ij}(-\omega_1; \omega_1) = \langle\langle \mu_i; V_j(\omega_1)\rangle\rangle_{\omega_1} =
$$
$$
\sum_k \{ \frac{\langle \Psi_0|\mu_i|\Psi^{(k)}\rangle\langle \Psi^{(k)}|V_j(\omega_1)|\Psi_0\rangle}{\omega_1 - \omega_k} - \frac{\langle \Psi_0|V_j(\omega_1)|\Psi^{(k)}\rangle\langle \Psi^{(k)}|\mu_i|\Psi_0\rangle}{\omega_1 + \omega_k} \} \ .
$$

$$(2.48)$$

Similarily, the quadratic response function defines the first hyperpolarizability β:

$$\beta_{ijk}(-\omega_1 - \omega_2; \omega_1, \omega_2) = \langle\langle \mu_i; V_j(\omega_1); V_k(\omega_2)\rangle\rangle_{\omega_1,\omega_2} =$$

$$\sum_{k,n} \{ \frac{\langle\Psi_0|\mu_i|\Psi^{(k)}\rangle \left(\langle\Psi^{(k)}|V_j(\omega_1)|\Psi^{(n)}\rangle - \delta_{kn}\langle\Psi_0|V_j(\omega_1)|\Psi_0\rangle\right) \langle\Psi^{(n)}|V_k(\omega_2)|\Psi_0\rangle}{(\omega_1 + \omega_2 - \omega_k)(\omega_2 - \omega_n)}$$

$$+ \quad \frac{\langle\Psi_0|V_k(\omega_2)|\Psi^{(n)}\rangle \left(\langle\Psi^{(n)}|V_j(\omega_1)|\Psi^{(k)}\rangle - \delta_{kn}\langle\Psi_0|V_j(\omega_1)|\Psi_0\rangle\right) \langle\Psi^{(k)}|\mu_i|\Psi_0\rangle}{(\omega_1 + \omega_2 + \omega_k)(\omega_2 + \omega_n)}$$

$$- \quad \frac{\langle\Psi_0|V_j(\omega_1)|\Psi^{(k)}\rangle \left(\langle\Psi^{(k)}|\mu_i|\Psi^{(n)}\rangle - \delta_{kn}\langle\Psi_0|\mu_i|\Psi_0\rangle\right) \langle\Psi^{(n)}|V_k(\omega_2)|\Psi_0\rangle}{(\omega_1 + \omega_k)(\omega_2 - \omega_n)} \} \ .$$

$$(2.49)$$

assuming that the summation indices run over both ground and excited states. If we exclude the ground state from the summation, the resulting expressions contain several more terms, called "renormalization terms" [31, 32].

SCF linear and quadratic response functions were derived for the first time in 1961 [33], while the first multiconfigurational (MCSCF) formulation of linear response was presented by Yeager and Jørgensen [34] and independently by Dalgaard [35]. A more general formulation of the MCSCF linear, quadratic and cubic response functions was given by Olsen *et al* [29]. Response functions have also been derived for other wavefunctions: linear response has been obtained for the MBPT(2) wavefunction in the polarizator propagator formalism [36]. Also, a coupled-cluster wavefunction has been used extensively to determine response functions. The linear coupled-cluster response equations have been formulated by Monkhorst [37] and Dalgaard and Monkhorst [38] and extended to quadratic response and applied to calculations of polarizability and hyperpolarizability by Koch and Jørgensen [39, 40].

CHAPTER 3

COMPUTATIONAL METHODS USING COUPLED-CLUSTER
WAVEFUNCTION

3.1 Rayleigh-Schrödinger Perturbation Theory Based Methods

In this chapter we will derive the expressions for linear polarizability and first and second-order hyperpolarizabilities in the presence of a static electric field. Consequently we will present the derivation of the time or frequency dependent first polarizability and show that the only difference between static and dynamic expressions is the presence of the frequency factor in the resolvent. The subsequent treatment of higher-order properties and new methods will be based on the time-independent formalism with frequency components inserted directly into the static expressions.

We will start by defining our Schrödinger equation as

$$H\Psi = E\Psi$$

$$(H_0 + V)\Psi = E\Psi \ . \tag{3.1}$$

where H_0 is the unperturbed Hamiltonian satisfying the equation

$$H_0\Phi_0 = E_0\Phi_0 \tag{3.2}$$

and V is the perturbation (response of the system to the external electric field at frequency $\omega = 0$).

To define our methods we will rearrange the equation (3.1) by adding an arbitrary factor λ:

$$(H_0 + V + \lambda)\Psi = (E - \lambda)\Psi \tag{3.3}$$

17

Considering Eq. (3.2) and assuming intermediate normalization ($\langle \Phi_0 | \Psi \rangle = 0$) we may write Eq. (3.3) as

$$(\lambda - H_0)\, \Psi = (V - E - \lambda)\, \Psi \tag{3.4}$$

Assigning different values to the parameter λ leads to various types of a perturbation expansion. However, we have to restrict the choice of λ to values different from the eigenvalues of H_0 in the $\Psi - \Phi_0$ space (also known as the Q-space, orthogonal to the subspace P which we choose to be Ψ_0). The reason for such a restriction is to allow for the inverse of $\hat{Q}\,(\lambda - H_0)\,\hat{Q}\Psi$ in a modified Schrödinger equation

$$\hat{Q}\,(\lambda - H_0)\,\hat{Q}\Psi = \hat{Q}\,(V - E + \lambda)\,\Psi \tag{3.5}$$

obtained from Eq. (3.4) by using the indempotency of $\hat{Q}$ and the fact that $\hat{Q}$ commutes with H_0. The inverse of $\hat{Q}\,(\lambda - H_0)\,\hat{Q}\Psi$ is also defined as the *resolvent operator* [41]

$$R_0(\lambda) = \frac{\hat{Q}}{\lambda - H_0} = \sum_i{}' \frac{|\Phi_i\rangle\langle\Phi_i|}{(\lambda - E_i)} \tag{3.6}$$

Substituting $\Psi = \Phi_0 + \hat{Q}\Psi$ and using the above definition of the resolvent we can rewrite Eq.(3.5) to read:

$$
\begin{aligned}
\Psi &= \Phi_0 + R_0(\lambda)\,(V - E + \lambda)\,\Psi \\
&= \Phi_0 + R_0(\lambda)\,(V - E + \lambda) + R_0(\lambda)\,(V - E + \lambda) = \cdots \\
&= \sum_{i=0}^{\infty}\{R_0(\lambda)\,(V - E + \lambda)\}^i \Psi_0
\end{aligned}
\tag{3.7}
$$

If we define the total perturbed energy as $E = E_0 + \Delta E$, we can then evaluate the perturbation energy as

$$\Delta E = \sum_{i=0}^{\infty} \langle \Phi_0 | V \{R_0(\lambda)\,(V - E + \lambda)\}^i | \Phi_0 \rangle \ . \tag{3.8}$$

The Eq.(3.8) allows us to calculate the perturbed energies knowing only the ground state wavefunction.

All the methods utilizing the perturbation expansion to treat excitations and properties were based on the Rayleigh-Schrödinger perturbation theory (RSPT), for which we define the lambda parameter (3.4) to be the ground state energy $\lambda = E_0$.

To apply RSPT to our purpose we will use the order-by-order expansion, followed by the zeroth-order expansion of resulting expressions, in order to get equations that are explicitly dependent only on the ground state wavefunction. We start with expanding the perturbed wavefunction and energy in a power series around the unperturbed values:

$$
\begin{aligned}
\Psi &= \Phi + \chi = \Phi^{(0)} + \kappa \Phi^{(1)} + \kappa^2 \Phi^{(2)} + \ldots, \\
E &= E^{(0)} + \Delta E = E^{(0)} + \kappa E^{(1)} + \kappa^2 E^{(2)} + \ldots.
\end{aligned}
\tag{3.9}
$$

By using the coupled-cluster parametrization for the ground and excited states (EOM-CC states), we can redefine the wavefunction

$$
\Psi_{cc} = e^T |0\rangle
\tag{3.10}
$$

and our Hamiltonian

$$
\bar{H} \equiv e^{-T} H_N e^T = \left(H_N e^T \right)_c = \bar{H}_N + \kappa \bar{V} .
\tag{3.11}
$$

We will refer to $\bar{H}$ as a similarity-transformed Hamiltonian. H_N is the normal-order Hamiltonian ($H_N = H - \langle 0|H|0\rangle$). The ground state $|0\rangle$ is a reference determinant. The similarity transformation is non-unitary and therefore the resulting Hamiltonian is no longer hermitian. Hence, the bra and ket wavefunctions are no longer simply orthogonal or each others conjugate, but instead they form a

biorthogonal basis [20]:

$$\langle\psi_0|L_k R_l|\psi_0\rangle = C\delta_{kl}$$

(3.12)

In the EOM method, we choose $L_0 = (1 + \Lambda)$, $R_0 = 1$ and $C=1$ for the ground state, where Λ is a deexcitation operator complementary to the excitation operator T [42]. We also partition our space into three subspaces: the ground state (Fermi vacuum) $|0\rangle\langle0|$, the space of single and double excitations $|\mathbf{h}\rangle\langle\mathbf{h}|$ (because we work within the CCSD approximation; had we used a more rigorous CCSDT method, this subspace would contain triple excitations) and the remainder - all higher excitations $|\mathbf{f}\rangle\langle\mathbf{f}|$ Together all three subspaces form a full space spanned by the operator $\bar{H}$.

It is noteworthy to mention that the above formulation satisfies the generalized Hellmann-Feynman theorem [42]:

$$\frac{d}{d\kappa}\langle0|(1+\Lambda)\bar{H} + \kappa\bar{V}|0\rangle = \langle0|(1+\Lambda)\bar{V}|0\rangle$$

(3.13)

Rewritting the Schrödinger equation (3.1) with

$$\hat{H} = \hat{H}_0 + \kappa\hat{V},$$

(3.14)

we get

$$\left(\hat{H}_0 + \kappa\hat{V} - E_n^{(0)} - \kappa E^{(1)} - \kappa^2 E^{(2)} - \ldots\right)\left(\Phi^{(0)} + \kappa\Phi^{(1)} + \kappa^2\Phi^{(2)} + \ldots\right) = 0.$$

(3.15)

Equating coefficients of equal powers of κ gives

$$\left(\hat{H}_0 - E^{(0)}\right)\Phi^{(m)} = \left(E^{(1)} - \hat{V}\right)\Phi^{(m-1)} + \sum_{l=0}^{m-2} E^{(m-l)}\Phi^{(l)},$$

$$\left(E^{(0)} - \hat{H}_0\right)\Phi^{(m)} = \hat{V}\Phi^{(m-1)} - \sum_{l=0}^{m-1} E^{(m-l)}\Phi^{(l)}$$

(3.16)

for κ^m (mth-order equation). After applying the ground state left eigenvector and expressing the perturbed wavefunctions in terms of the zero order wavefunction we obtain

$$\langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right)|\Phi^{(1)}\rangle = \langle\Phi_0|\hat{W}|\Phi_0\rangle\,, \tag{3.17}$$

$$\langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right)|\Phi^{(2)}\rangle = \langle\Phi_0|\hat{W}|\Phi^{(1)}\rangle + E^{(2)}|\Phi^{(0)}\rangle$$
$$= \langle\Phi_0|\hat{W}R_0(E_0)\hat{V}|\Phi_0\rangle + E^{(2)}|\Phi_0\rangle\,, \tag{3.18}$$

$$\langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right)|\Phi^{(3)}\rangle = \langle\Phi_0|\hat{W}|\Phi^{(2)}\rangle + E^{(3)} + E^{(2)}\langle\Phi_0|\Phi^{(1)}\rangle$$
$$= \langle\Phi_0|\hat{W}R_0(E_0)\hat{W}R_0(E_0)\hat{V}|\Phi_0\rangle + E^{(3)} + E^{(2)}\langle\Phi_0|R_0(E_0)\hat{V}|\Phi_0\rangle\,, \tag{3.19}$$

$$\langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right)|\Phi^{(4)}\rangle = \langle\Phi_0|\hat{W}|\Phi^{(3)}\rangle + E^{(3)} + E^{(2)}\langle\Phi_0|\Phi^{(1)}\rangle$$
$$= \langle\Phi_0|\hat{W}R_0(E_0)\hat{W}R_0(E_0)\hat{W}R_0(E_0)\hat{V}|\Phi_0\rangle + E^{(4)} + E^{(3)}\langle\Phi_0|R(E)_0\hat{V}|\Phi_0\rangle$$
$$+ E^{(2)}\langle\Phi_0|R_0(E_0)\hat{V}R_0(E_0)\hat{V}|\Phi_0\rangle + E^{(2)}\langle\Phi_0|\hat{V}R_0(E_0)R_0(E_0)\hat{V}|\Phi_0\rangle\,. \tag{3.20}$$

In the above equations $\hat{W} = \hat{V} - E^{(1)}$ and $R_0(E_0)$ is the RS resolvent operator

$$R_0(E_0) = \sum_{ij}|\Phi_i\rangle\langle\Phi_i|E_0 - \bar{H}_{ij}|\Phi_j\rangle\langle\Phi_j| \tag{3.21}$$

defined for the non-diagonal $\bar{H}$ Hamiltonian. The RSPT resolvent contains only the zeroth-order energy and thus evaluating equations (3.17) to (3.20) is straightforward and does not involve any iterating procedures.

The coupled-cluster perturbed wavefunction $|\Phi(n)\rangle$ can be written in terms of the unperturbed ground state wavefunction with the excitation operators being actually perturbed:

$$|\Phi^{(1)}\rangle_{cc} = T^{(1)}|\Phi_0\rangle\,,$$
$$|\Phi^{(2)}\rangle_{cc} = T^{(2)} + T^{(1)}T^{(1)}|\Phi_0\rangle\,,$$

$$|\Phi^{(3)}\rangle_{cc} = T^{(3)} + T^{(2)}T^{(1)} + T^{(1)}T^{(1)}T^{(1)}|\Phi_0\rangle \,,$$

$$|\Phi^{(4)}\rangle_{cc} = T^{(4)} + T^{(3)}T^{(1)} + T^{(2)}T^{(2)} + T^{(2)}T^{(1)}T^{(1)} + T^{(1)}T^{(1)}T^{(1)}T^{(1)}|\Phi_0\rangle \,.$$

$$(3.22)$$

Applying the above results to the zero order expansions in Eqs. (3.17) to (3.20) and noting that $\langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right)T^{(n)}|\Phi_0\rangle = 0$, $\langle\Phi_0| = \langle 0|(1 + \Lambda)$ and $|\Phi_0\rangle = |0\rangle$ we get

$$E^{(1)} = \langle 0|(1 + \Lambda)\hat{V}|0\rangle \,, \tag{3.23}$$

$$E^{(2)} = \langle 0|(1 + \Lambda)\hat{W}R_0(E_0)\hat{V}|0\rangle + \langle 0|(1 + \Lambda)\left(\hat{H}_0 - E^{(0)}\right)T^{(1)}T^{(1)}|0\rangle \,, \tag{3.24}$$

$$E^{(3)} = \langle 0|(1 + \Lambda)\hat{W}R_0(E_0)\hat{W}R_0(E_0)\hat{V}|0\rangle +$$
$$E^{(2)}\langle 0|(1 + \Lambda)R_0(E_0)\hat{V}|0\rangle + \langle 0|(1 + \Lambda)\left(\hat{H}_0 - E^{(0)}\right)T^{(1)}T^{(1)}T^{(1)}|0\rangle +$$
$$\langle 0|(1 + \Lambda)\left(\hat{H}_0 - E^{(0)}\right)T^{(2)}T^{(1)}|0\rangle \,, \tag{3.25}$$

$$E^{(4)} = \langle 0|(1 + \Lambda)\hat{W}R_0(E_0)\hat{W}R_0(E_0)\hat{W}R_0(E_0)\hat{V}|0\rangle +$$
$$E^{(3)}\langle 0|(1 + \Lambda)R_0(E_0)\hat{V}|0\rangle + E^{(2)}\langle 0|(1 + \Lambda)R_0(E_0)\hat{W}R_0(E_0)\hat{V}|0\rangle +$$
$$E^{(2)}\langle 0|(1 + \Lambda)\hat{W}R_0(E_0)R_0(E_0)\hat{V}|0\rangle +$$
$$\langle 0|(1 + \Lambda)\left(\hat{H}_0 - E^{(0)}\right)T^{(1)}T^{(1)}T^{(1)}T^{(1)}|0\rangle +$$
$$\langle 0|(1 + \Lambda)\left(\hat{H}_0 - E^{(0)}\right)T^{(2)}T^{(1)}T^{(1)}|0\rangle +$$
$$\langle 0|(1 + \Lambda)\left(\hat{H}_0 - E^{(0)}\right)T^{(3)}T^{(1)}|0\rangle +$$
$$\langle 0|(1 + \Lambda)\left(\hat{H}_0 - E^{(0)}\right)T^{(2)}T^{(2)}|0\rangle \,. \tag{3.26}$$

The above equations contain three classes of terms: the leading term is a sum-over-states-like term which is the most significant numerically and has its direct equivalent in the polarizator propagator formalism [27, 28, 29]. The second category of terms is the renormalization terms coming from the perturbation expansion. They contain unlinked diagrams of type $E^{(n)} * \langle 0|f(R, V)|0\rangle$ which cancel

unlinked terms showing up in the leading term, due to the structure of both the perturbation operator $(V - E^{(1)})$ and the CI-like operator Λ. The last part of the renormalization terms is the "multiple-T", higher-order terms coming from the expansion of the perturbed coupled-cluster wavefunction. They describe effects of higher (triple, quadruple etc.) excitations that occur in the leading SOS-like term but are not adequately accounted for in the CCSD partitioning of the full space. The numerical significance of the renormalization terms is discussed elsewhere in this dissertation.

We can now utilize Eqs. (2.25) and (2.32) and write down the RSPT equations for linear polarizability as well as for the first and second hyperpolarizability for a case where the higher-order renormalization terms are neglected:

$$\alpha(0;0) = 2\langle 0|(1+\Lambda)\hat{W}R_0(E_0)\hat{V}|0\rangle \,, \tag{3.27}$$

$$\begin{aligned} \beta(0;,0,0) &= 6\langle 0|(1+\Lambda)\hat{W}R_0(E_0)\hat{W}R_0(E_0)\hat{V}|0\rangle + \\ &\quad \alpha(0;0)\langle 0|(1+\Lambda)R_0(E_0)\hat{V}|0\rangle \,, \end{aligned}$$

$$\tag{3.28}$$

$$\begin{aligned} \gamma(0;0,0,0) &= 24\langle 0|(1+\Lambda)\hat{W}R_0(E_0)\hat{W}R_0(E_0)\hat{W}R_0(E_0)\hat{V}|0\rangle + \\ &\beta(0;0,0)\langle 0|(1+\Lambda)R_0(E_0)\hat{V}|0\rangle + \alpha(0;0)\langle 0|(1+\Lambda)R_0(E_0)\hat{W}R_0(E_0)\hat{V}|0\rangle + \\ &\alpha(0;0)\langle 0|(1+\Lambda)\hat{W}R_0(E_0)R_0(E_0)\hat{V}|0\rangle \,. \end{aligned}$$

$$\tag{3.29}$$

3.1.1 Time-Dependent Derivation of the First Polarizability Expressions

Properties can usually be evaluated from the derivative of energy associated with a wave function, subject to an external perturbation. For time-independent

perturbations this is straightforward. For example, dipole-moments, static polarizabilities and hyperpolarizabilities are defined as the first, second and third derivatives of energy which are proportional to the zeroth-, first- and second-order responses of a molecule to a static electric field. However, a straightforward extension of energy derivative methods to time-dependent perturbations is not as apparent, because the corresponding energy is not uniquely defined. Hence, the starting point of our derivation is the time dependent dipole moment which is well defined and unique.

The time-dependent dipole moment is given by

$$\mu\left(t\right) = \left\langle \Psi\left(t\right) \left|\hat{\mu}\right| \Psi\left(t\right)\right\rangle \tag{3.30}$$

where $\left|\Psi\left(t\right)\right\rangle$ satisfies the time-dependent Schrödinger equation

$$i\frac{\partial\left|\Psi\left(t\right)\right\rangle}{\partial t} = \bar{H}\left(t\right)\left|\Psi\left(t\right)\right\rangle \tag{3.31}$$

and is assumed to be normalized at time $t = 0$, and hence at all times. To define polarizabilities, hyperpolarizibilities and so forth, let us consider the field dependent Hamiltonian

$$
\begin{aligned}
H\left(t\right) &= H_0 + \sum_a d\omega_a \varepsilon_a\left(\omega_a\right) \hat{\mu}_a e^{-i\omega_a t} \\
&= H_0 + V\left(t\right)
\end{aligned}
\tag{3.32}
$$

where H_0 is the usual molecular Hamiltonian, $\hat{\mu}_a$ denotes the three Cartesian components of the dipole operator, while $\varepsilon_a\left(\omega_a\right)$ indicates the respective components of the frequency-dependent field strength. (Every integration, either in time or in frequency is accompanied by a factor $1/\sqrt{2\pi}$. We absorb this factor in our integral sign to facilitate the notation.

At time $t = 0$ we assume that the state $\left|\Psi\left(0\right)\right\rangle$ is the ground state (or possibly another stationary state) of the field independent molecular Hamiltonian H_0.

Under these conditions the polarizability and higher polarizabilities (with respect to the state at time $t = 0$) can be defined as the expansion coefficients of the time-dependent dipole moment

$$\mu_A (t) = \mu_A^{(0)} + \sum_a \int d\omega_a \alpha_{Aa} (\omega_a) \varepsilon (\omega_a) e^{-i\omega_a t} +$$

$$\frac{1}{2!} \sum_{a,b} \int d\omega_a d\omega_b \beta_{Aab} (\omega_a, \omega_b) \varepsilon (\omega_a) \varepsilon (\omega_b) e^{-i(\omega_a + \omega_b)t} + ... \qquad (3.33)$$

Here, we adopt the convention [15], using upper case letters for the component under consideration and lower case letters to indicate components that are summed over. For future reference, the Fourier transform of $\mu_A (t)$ reads

$$
\begin{aligned}
\mu_A (\omega) &= \int_{-\infty}^{\infty} \mu_A (t) e^{i\omega t} dt \\
&= \mu_A^{(0)} \delta (\omega) + \sum_a \int d\omega_a \alpha_{Aa} (\omega_a) \varepsilon_a (\omega_a) \delta (\omega - \omega_a) + \\
&\quad 1/2! \sum_{a,b} \int_{-\infty}^{\infty} d\omega_a d\omega_b \beta_{Aab} (\omega_a, \omega_b) \varepsilon_a (\omega_a) \varepsilon_b (\omega_b) \delta (\omega - \omega_a - \omega_b) + ...
\end{aligned}
$$

$$(3.34)$$

It follows that the polarizability can be obtained as

$$\alpha_{AB} (\omega_B) = \int_{-\infty}^{\infty} d\omega \frac{\partial \mu_A (\omega)}{\partial \varepsilon (\omega_B)} \bigg|_{\mathbf{E}=0} \qquad (3.35)$$

where $\mathbf{E}$ indicates all components of the field strength. The first hyperpolarizability is given by

$$\beta_{ABC} (\omega_B, \omega_C) = \beta_{ACB} (\omega_C, \omega_B) = \int_{-\infty}^{\infty} d\omega \frac{\partial \mu_A (\omega)}{\partial \varepsilon_B (\omega_B) \partial \varepsilon_C (\omega_C)} \bigg|_{\mathbf{E}=0} \qquad (3.36)$$

The wave-function $|\Psi (t)\rangle$ that defines the time- or frequency dependent dipole moment satisifies the time-dependent Schrodinger equation corresponding to the complete, field dependent, Hamiltonian. This wave function (and the time-dependent

dipole moment) can be expanded in orders of the field, and this will yield expressions for the polarizability and hyperpolarizabilities. If we assume that all eigenstates of the molecular Hamiltonian are known (at least formally), we can obtain in this way the familiar sum over states expressions for the polarizability and so forth. Alternatively, we can assume a parameterization for the complete field-dependent wave function, which is then subject to a perturbation expansion. This leads directly to equations for the perturbed amplitudes, which in turn define the quantities of interest. One possible parameterization is, of course, the exponential coupled-cluster ansatz, which is the focus of this thesis. The above approach to polarizabilities (or hyperpolarizabilities and so forth) does not apply directly to the coupled-cluster formalism, however. The reason is that the time-dependent wave-function in the CC formalism is not normalized to unity but rather satisfies intermediate normalization

$$|\Psi_{CC}(t)\rangle = e^{T(t)}|\Phi_0\rangle \rightarrow \langle\Phi_0|\Psi_{CC}(t)\rangle = 1 \qquad (3.37)$$

The exact CC wave-function is proportional to $|\Psi(t)\rangle$, where the proportionality factor is in general complex. Let us write

$$|\Psi(t)\rangle = |\Psi_{CC}(t)\rangle e^{-i\varphi(t)} \qquad (3.38)$$

where the normalization factor is defined as

$$e^{-i\varphi(t)} = \langle\Phi_0|\Psi(t)\rangle \qquad (3.39)$$

Substituting this expression in the time-dependent Schrödinger equation, and multiplying by $e^{i\varphi(t)}$ we obtain

$$i\frac{\partial}{\partial t}|\Psi_{CC}(t)\rangle + \frac{\partial\varphi(t)}{\partial t}|\Psi_{CC}(t)\rangle = H|\Psi_{CC}(t)\rangle \qquad (3.40)$$

If we multiply in addition by $e^{-T(t)}$ we find

$$i\frac{\partial T}{\partial t}\left|0\right\rangle + \frac{\partial \varphi}{\partial t}\left|0\right\rangle = \bar{H}\left(t\right)\left|0\right\rangle \tag{3.41}$$

where $\bar{H}\left(t\right) = e^{-T(t)}He^{T(t)}$. It may be appreciated that the equations for T are completely decoupled from the equation for the phase

$$\begin{aligned}\left\langle q\right|\bar{H}\left(t\right) - i\frac{\partial T}{\partial t}\left|0\right\rangle &= 0 \\ \frac{\partial \varphi}{\partial t} &= \left\langle 0\right|\bar{H}\left(t\right)\left|0\right\rangle\end{aligned} \tag{3.42}$$

The analogy with time-independent CC theory is evident. The quantity $\frac{\partial \varphi}{\partial t}$ is called the quasi-energy, and it has been observed that polarizabilities and so forth can be obtained from differentiating this quantity [38, 37, 15, 13, 16]. The relation between the quasi-energy and the quantities of interest is not very transparent in our opinion; however, so we prefer to not use the quasi-energy. The time-dependent dipole moment in terms of the CC wave-function is defined as the expectation value,

$$\frac{e^{i\varphi(t)}\left\langle \Psi_{CC}\left(t\right)\right|\hat{\mu}_A\left|\Psi_{CC}\left(t\right)\right\rangle e^{-i\varphi(t)}}{e^{i\varphi(t)}\left\langle \Psi_{CC}\left(t\right)\left|\Psi_{CC}\left(t\right)\right\rangle e^{-i\varphi(t)}} \equiv \left\langle \tilde{\Psi}_{CC}\left(t\right)\right|\hat{\mu}_A\left|\Psi_{CC}\left(t\right)\right\rangle \tag{3.43}$$

The state

$$\left\langle \tilde{\Psi}_{CC}\left(t\right)\right| = \frac{\left\langle \Psi_{CC}\left(t\right)\right|}{\left\langle \Psi_{CC}\left(t\right)\left|\Psi_{CC}\left(t\right)\right\rangle} \tag{3.44}$$

by definition satisfies the normalization condition

$$\left\langle \tilde{\Psi}_{CC}\left(t\right)\left|\Psi_{CC}\left(t\right)\right\rangle = 1 \tag{3.45}$$

and it can be conveniently parameterized as

$$\left\langle \tilde{\Psi}_{CC}\left(t\right)\right| = \left\langle \Phi_0\right|\left(1 + \Lambda\left(t\right)\right)e^{-T(t)} \tag{3.46}$$

where $\Lambda\left(t\right)$ is a de-excitation operator introduced in analogy with CC derivative theory [43, 42]. The normalization condition is satisfied trivially for all values of

the parameters determining the operators $\Lambda(t)$ and $T(t)$. The state $\langle \tilde{\Psi}_{CC}(t) |$ is related to the true Schrödinger bra as $\langle \Psi(t) | = e^{i\varphi(t)} \langle \tilde{\Psi}_{CC}(t) |$ and the time evolution of this state is of course determined by the Schrödinger equation

$$-i \frac{\partial}{\partial t} \langle \Psi(t) | = \langle \Psi(t) | H \qquad (3.47)$$

If we substitute the parameterization for $\langle \tilde{\Psi}(t) |$ in the Schrödinger equation and multiply by $e^{-i\varphi(t)}$ and e^T from the right, we find

$$\langle 0 | (1 + \Lambda(t)) \left[\bar{H}(t) - i \frac{\partial T}{\partial t} - \frac{\partial \varphi}{\partial t} \right] + i \langle 0 | \frac{\partial \Lambda(t)}{\partial t} = 0 \,. \qquad (3.48)$$

Projecting on $|0\rangle$ and $|q\rangle = \hat{q}|0\rangle$, we obtain

$$
\begin{aligned}
\frac{\partial \varphi}{\partial t} &= \langle 0 | \bar{H}(t) | 0 \rangle + \langle 0 | \Lambda(t) \left[\bar{H}(t) - i \frac{\partial T}{\partial t} \right] | 0 \rangle \\
&= \langle 0 | \bar{H}(t) | 0 \rangle
\end{aligned}
\qquad (3.49)
$$

and

$$
\langle 0 | (1 + \Lambda(t)) \left[\bar{H}(t), q \right] | 0 \rangle + i \langle 0 | \frac{\partial \Lambda}{\partial t} | q \rangle +
$$
$$
\langle 0 | (1 + \Lambda(t)) \hat{q} \left\{ \bar{H}(t) - i \frac{\partial T}{\partial t} - \frac{\partial \varphi}{\partial t} \right\} | 0 \rangle = 0 \,. \qquad (3.50)
$$

The last term in this equation vanishes because the CC equations are satisfied (this is true also if T is truncated). Let us summarize our basic equations obtained so far:

$$\mu(t) = \langle 0 | (1 + \Lambda(t)) e^{-T(t)} \hat{\mu} e^{T(t)} | 0 \rangle = \langle 0 | (1 + \Lambda(t)) \hat{\mu}(t) | 0 \rangle \,, \qquad (3.51)$$

$$\langle q | \left(\bar{H}(t) - i \frac{\partial T}{\partial t} \right) | 0 \rangle = 0 \,, \qquad (3.52)$$

$$\langle 0 | (1 + \Lambda(t)) \left[\bar{H}(t), \hat{q} \right] | 0 \rangle + i \langle 0 | \frac{\partial \Lambda}{\partial t} | q \rangle = 0 \,. \qquad (3.53)$$

In addition, we have an equation for the phase factor that establishes the connection between our CC states and the true (normalized) wave functions

$$\frac{\partial \varphi}{\partial t} = \langle 0 | \bar{H}(t) | 0 \rangle \tag{3.54}$$

However, this quantity will not play any further role in our derivation. To obtain a perturbation expansion for the time-dependent dipole moment, we assume a perturbation expansion for the cluster operator T and the operator Λ.

$$T(\kappa, t) = \sum_{n=0}^{\infty} \kappa^n T^{(n)}(t) \tag{3.55}$$

$$\Lambda(\kappa, t) = \sum_{n=0}^{\infty} \kappa^n \Lambda^{(n)}(t) \tag{3.56}$$

To keep the notation compact we also introduce an expansion for

$$\bar{H}(t) = \sum_{n=0}^{\infty} \kappa^n \bar{H}^{(n)}(t) \tag{3.57}$$

The components $\bar{H}^{(n)}$ are defined in terms of H_0, V and the various $T^{(m)}$, for example

$$
\begin{aligned}
\bar{H}^{(0)} &= e^{-T^{(0)}} H_0 e^{T^{(0)}} \\
\bar{H}^{(1)} &= \left[\bar{H}^{(0)}, T^{(1)} \right] + e^{-T^{(0)}} V e^{T^{(0)}} \\
&\vdots \\
\bar{H}^{(n)} &= \left[\bar{H}^{(0)}, T^{(n)} \right] + \bar{H}^{(n/n-1)}
\end{aligned}
\tag{3.58}
$$

For future convenience we have introduced $\bar{H}^{(n/m)}$ to denote all terms in $\bar{H}^{(n)}$ that can be obtained by connecting cluster operators of order $\leq m$ to $H = H_0 + V$. This notation allows us to write explicit equations for $T^{(n)}$, for $n > 0$

$$\langle q | \left[\bar{H}^{(0)}, T^{(n)}(t) \right] - i \frac{\partial T^{(n)}}{\partial t} | 0 \rangle = -\langle q | \bar{H}^{(n/n-1)}(t) | 0 \rangle \tag{3.59}$$

These equations can be solved hierarchically. Similarly the equations for $\Lambda^{(n)}$ can be written

$$\langle 0|\Lambda^{(n)}(t)\left[\bar{H}^{(0)},\hat{q}\right]|0\rangle + i\langle 0|\frac{\partial \Lambda^{(n)}}{\partial t}|q\rangle =$$

$$-\langle 0|\left(1+\Lambda^{(0)}\right)\left[\bar{H}^{(n)}(t),\hat{q}\right]|0\rangle - \sum_{k=1}^{n-1}\langle 0|\Lambda^{(k)}(t)\left[\bar{H}^{(n-k)}(t),\hat{q}\right]|0\rangle. \quad (3.60)$$

Again these equations can be solved hierarchically. The equations for $\Lambda^{(n)}$, require the solution of perturbed amplitudes T up to and including $T^{(n)}$. The zeroth order equations are the usual time-independent T and Λ equations

$$\langle q|\bar{H}^{(0)}|0\rangle = 0 \quad (3.61)$$

and

$$\langle 0|\Lambda\left[\bar{H}^{(0)},\hat{q}\right]|0\rangle = -\langle 0|\bar{H}^{(0)}|q\rangle. \quad (3.62)$$

The higher order equations are best solved in the frequency domain. If we introduce Fourier transforms

$$T(\omega) = \int e^{i\omega t}T(t)\,dt \quad (3.63)$$

the equation for $T^{(n)}(\omega)$ can be written

$$\langle q|\left[\bar{H}^{(0)},T^{(n)}(\omega)\right] + \omega T^{(n)}(\omega)|0\rangle = -\langle q|\bar{H}^{(n/n-1)}(\omega)|0\rangle. \quad (3.64)$$

With the operator $\langle q|\left[\bar{H}^{(0)},p\right]|0\rangle + \omega\delta_{pq}$ we associate its inverse, the resolvent $\hat{R}^0(\omega)$, that only acts in the space of excited determinants. Hence we can write

$$\langle q|T^{(n)}(\omega)|0\rangle = -\langle q|\hat{R}^0(\omega)\bar{H}^{(n/n-1)}(\omega)|0\rangle. \quad (3.65)$$

The resolvent has the very useful property that when acting on a connected operator in its right, the result is again connected. We will see that the structure

of the whole approach will be intrinsically connected. The quantity

$$\langle q| \bar{H}^{(n/n-1)}(\omega)|0\rangle = \int e^{i\omega t}\langle q|\bar{H}^{(n/n-1)}(t)|0\rangle dt \tag{3.66}$$

is in general a complicated expression that involves the Fourier transform of a product of functions of time (T-amplitudes, a time-dependent perturbation etc.). Each of these elementary functions have a Fourier transform, and the total transform can be written as a generalized convolution, e.g.

$$\int f(t)\,g(t)\,h(t)\,e^{i\omega t}dt =$$
$$\int\int\int d\omega_1 d\omega_2 d\omega_3 \int f(\omega_1)\,g(\omega_2)\,h(\omega_3)\,e^{i(\omega-\omega_1-\omega_2-\omega_3)t}dt$$
$$= \int\int\int d\omega_1 d\omega_2 d\omega_3 f(\omega_1)\,g(\omega_2)\,h(\omega_3)\,\delta(\omega-\omega_1-\omega_2-\omega_3)\ . \tag{3.67}$$

We note that these type of expressions have precisely the same form as the polarizibilities and so forth, and this will therefore provide an easy connection. The equation for $\Lambda^{(n)}$ takes the form

$$\langle 0|\Lambda^{(n)}(\omega)\left[\bar{H}^{(0)},q\right]|0\rangle - \omega\langle 0|\Lambda^{(n)}(\omega)|q\rangle =$$
$$- \langle 0|\left(1+\Lambda^{(0)}\right)\left[\bar{H}^{(n)}(\omega),q\right]|0\rangle$$
$$- \sum_{k=1}^{n-1}\langle 0|\Lambda^{(k)}(\omega)\left[\bar{H}^{(n-k)}(\omega),q\right]|0\rangle\ . \tag{3.68}$$

Using the resolvent, the solution can be written

$$\langle 0|\Lambda^{(n)}(\omega)|p\rangle = -\sum_q\sum_{k=0}^{n-1}\langle 0|\left(\delta_{k0}+\Lambda^{(k)}(\omega)\right)\left[\bar{H}^{(n-k)}(\omega),q\right]|0\rangle\hat{R}^0_{qp}(-\omega)\ . \tag{3.69}$$

The above equations are not the most convenient for application. One may manipulate further starting from the expression for the frequency dependent dipole moment and eliminating the frequency dependent Λ terms.

As mentioned before, the dynamic polarizibility is related to the first-order term in the dipole moment,

$$
\begin{aligned}
\alpha_{Aa}(\omega) &= \int d\omega_1 \frac{\mu_A^{(1)}(\omega_1)}{\partial \varepsilon_a(\omega)} = \langle 0|\left(1+\Lambda^{(0)}\right)\left[\bar{\mu}_A^{(0)}, T_a^{(1)}(\omega)\right]|0\rangle \\
&+ \langle 0|\Lambda_a^{(1)}(\omega)\,\bar{\mu}_A^{(0)}|0\rangle
\end{aligned} \tag{3.70}
$$

where

$$
\langle q|T^{(1)}(\omega)|0\rangle = -\langle q|\bar{R}_0(\omega)\,\bar{\mu}_a^{(0)}|0\rangle \tag{3.71}
$$

and

$$
\langle 0|\Lambda_a^{(1)}(\omega)|p\rangle = \langle 0|\left(1+\Lambda^{(0)}\right)\left[\bar{H}_a^{(1)}(\omega), q\right]|0\rangle \bar{R}_{qp}^0(-\omega) \ . \tag{3.72}
$$

Using

$$
\bar{R}^0(-\omega)\,\bar{\mu}_A^0|0\rangle = T_A^{(1)}(-\omega) \tag{3.73}
$$

and

$$
\bar{H}_a^{(1)}(\omega) = \bar{\mu}_a^{(0)} + \left[\bar{H}^{(0)}, T_a^{(1)}(\omega)\right] \tag{3.74}
$$

we find

$$
\begin{aligned}
\alpha_{Aa}(\omega) &= \langle 0|\left(1+\Lambda^{(0)}\right)\left[\bar{\mu}_A^{(0)}, T_a^{(1)}(\omega)\right]|0\rangle + \langle 0|\left(1+\Lambda^{(0)}\right)\left[\bar{\mu}_a^{(0)}, T_A^{(1)}(-\omega)\right]|0\rangle + \\
&\quad \langle 0|\left(1+\Lambda^{(0)}\right)\left[\left[\bar{H}^{(0)}, T_a^{(1)}(\omega)\right], T_A^{(1)}(-\omega)\right]|0\rangle
\end{aligned} \tag{3.75}
$$

which is a familiar expression for the polarizability in a CC framework [39]. We can rewrite Eq. (3.74) in the configuration basis [44] as

$$
\begin{aligned}
\alpha_{Aa}(\omega) &= \sum_{\mu,\nu}\langle 0|\left(1+\Lambda^{(0)}\right)\left[\bar{\mu}_A^{(0)} - \langle\bar{\mu}_A^{(0)}\rangle\right]|\mathbf{h}\rangle \mathbf{A}^{-1}(+\omega)\langle\mathbf{h}|\bar{\mu}_a^{(0)} - \langle\bar{\mu}_a^{(0)}\rangle|0\rangle + \\
&\quad \sum_{\mu,\nu}\langle 0|\left(1+\Lambda^{(0)}\right)\left[\bar{\mu}_A^{(0)} - \langle\bar{\mu}_A^{(0)}\rangle\right]|\mathbf{h}\rangle \mathbf{A}^{-1}(-\omega)\langle\mathbf{h}|\bar{\mu}_a^{(0)} - \langle\bar{\mu}_a^{(0)}\rangle|0\rangle + \\
&\quad \langle 0|\left(1+\Lambda^{(0)}\right)\left(\bar{H}^{(0)} - E_0\right)|\mathbf{f}\rangle\langle\mathbf{f}|T_a^{(1)}(\omega)\,T_A^{(1)}(-\omega)|0\rangle
\end{aligned} \tag{3.76}
$$

where

$$\mathbf{A}\left(\pm\omega\right) = \langle\mathbf{h}| \left(\bar{H}^{(0)} - E^{(0)} \pm \omega\right) |\mathbf{h}\rangle, \qquad (3.77)$$

where $|\mathbf{h}\rangle$ indicates the manifold of singly and doubly excited determinants. $\langle\bar{\mu}^{(0)}\rangle = \langle 0| (1 + \Lambda)\, \bar{\mu}^{(0)}|0\rangle$ and $|\mathbf{f}\rangle$ indicates all determinants that are higher than twofold excited. In the limit that the $|\mathbf{h}\rangle$ manifold is complete the quadratic term in Eq. (3.76) vanishes, or at the CCSD level the result is equivalent to Full CI for two electrons. Alternatively, we can adopt the "propagator" viewpoint [21], which defines the polarizability as

$$\alpha_{Aa}\left(\omega\right) = \sum_{l=0}^{1} \sum_{k \neq 0} \frac{\langle\tilde{\Psi}_0^{(0)}|\hat{\mu}_A^{(0)} - \langle\hat{\mu}_A^{(0)}\rangle|\Psi_k^{(0)}\rangle\langle\tilde{\Psi}_k^{(0)}|\hat{\mu}_A^{(0)} - \langle\hat{\mu}_A^{(0)}\rangle|\tilde{\Psi}_0^{(0)}\rangle}{\left(E_0^{(0)} - E_k^{(0)} + (-1)^l\,\omega\right)} \qquad (3.78)$$

where $\Psi_k^{(0)}$ and $E_k^{(0)}$, $k = 0, 1, \ldots$ are eigenfunctions and eigenvalues of the unperturbed zeroth-order Hamiltonian. The states $\Psi_k^{(0)}, \tilde{\Psi}_k^{(0)}$ form a complete biorthogonal set (i.e. $\langle\tilde{\Psi}_k^{(0)}|\Psi_l^{(0)}\rangle = \delta_{kl}$). By using the CC parametrization for the ground and excited states (EOM-CC states), we can rewrite Eq. (3.78) as

$$\alpha_{Aa}\left(\omega\right) = \sum_{l=0}^{1} \langle 0| (1 + \Lambda)\,| \left(\bar{\mu}_A^{(0)} - \langle\bar{\mu}_A^{(0)}\rangle\right) |\mathbf{h}\rangle\mathbf{A}^{-1}\left((-1)^l\,\omega\right)\langle\mathbf{h}|\bar{\mu}_A^{(0)}|0\rangle \qquad (3.79)$$

which amounts to exactly the first two terms of Eq. (3.76).

Equation (3.79) is also the same as Eq.(3.27) in the limiting static case, i.e. when $\omega = 0$. We can therefore safely assume, that the time-dependent derivation leads to expressions which are equivalent to the time-independent formulas, while being much more laborous and complicated.

However, extreme care has to be taken when going in oposite direction; from time-independent case to equations with frequency-dependence. Although general formulas remain the same, the presence of the frequency component causes the necessity to evaluate certain frequency dependent moments separately. The final property is not a sum of 24 identical moments as in case of second hyperpolarizability γ [Eq.(3.29)], but in general it becomes a sum of 24 different components,

each with its own structure of the frequency dependent resolvent. Of course, due to molecular symmetry, a great number of these components are identical and the general formulas for all the known electrooptic processes are well known [31, 45].

3.1.2 Role of the Renormalization Terms in the Sum-Over-States Expression

Butcher's formula for frequency-dependent polarizabilities in the notation of Bishop [32] is

$$X^n_{\alpha,\beta...i} \quad (-\omega_\sigma, \omega_1, \ldots \omega_n) = \mathbf{P}_{\alpha,\beta,...i} \sum_{a_1} \sum_{a_2} \cdots \sum_{a_n} \langle g \left| \overline{\mu}_\alpha \right| a_1 \rangle \left\langle a_1 \left| \overline{\mu}_\beta \right| a_2 \right\rangle$$

$$\ldots \langle a_n \left| \overline{\mu}_i \right| g \rangle \left[(\omega_{a_1} - \omega_\sigma)(\omega_{a_2} - \omega_\sigma + \omega_1) \cdots (\omega_{a_n} - \omega_n) \right]^{-1} \quad (3.80)$$

where $\mathbf{P}_{\alpha,\beta,...i}$ represents a summation over all forms obtained by simultaneously permuting pairs of dipole operators, $\overline{\mu}_i = \hat{\mu}_i - \langle g \left| \hat{\mu}_i \right| g \rangle$ and associated frequencies, ω_i. Also, $\omega_\sigma = \omega_1 + \omega_2 + \ldots + \omega_n$. Writing this expression in terms of the resolvent operator, where $|\mathbf{\Phi}\rangle = |g, a_1, a_2 \ldots a_n\rangle$,

$$R(\omega_x) = |\mathbf{\Phi}\rangle \langle \mathbf{\Phi}| E_0 - H_0 + \omega_x |\mathbf{\Phi}\rangle^{-1} \langle \mathbf{\Phi}| = \sum_k |\Phi_k\rangle \langle \Phi_k| (\omega_k - \omega_\sigma)^{-1} \quad (3.81)$$

$$X^n_{\alpha,\beta,...i} = \mathbf{P}_{a,\beta,...i} \langle g| \overline{\mu}_a R(-\omega_\sigma) \overline{\mu}_\beta R(\omega_1 - \omega_\sigma) \overline{\mu}_\gamma R(\omega_1 + \omega_2 - \omega_\sigma) \ldots \overline{\mu}_i R(-\omega_n) |g\rangle \ . \quad (3.82)$$

In the EOM-CC theory, we have separate right $\{\mathbf{r}\}$ and left $\{\mathbf{l}\}$ biorthogonal eigenstates of $\overline{H} = e^{-T} H e^T$ that form a resolution of the identity, $1 = |\mathbf{r}\rangle\langle\mathbf{l}|\mathbf{r}\rangle^{-1}\langle\mathbf{l}|$. For $k = 0$, $\langle 0| l_0 = \langle 0| (1 + \Lambda)$, $r_0 |0\rangle = |0\rangle$. Using the facts that $|\mathbf{\Phi}\rangle = e^T |\mathbf{r}\rangle \mathbf{S} = e^T |\mathbf{h}\rangle \mathbf{C}$ and $\langle\mathbf{\Phi}| = \tilde{\mathbf{S}} \langle\mathbf{l}| e^{-T} = \tilde{\mathbf{C}} \langle\mathbf{h}| e^{-T}$ where $|\mathbf{h}\rangle = |0, \mathbf{f}_1, \mathbf{f}_2, \ldots \mathbf{f}_n\rangle$ with $|0\rangle$ the Fermi vacuum state and $\mathbf{f}_1, \mathbf{f}_2, \ldots$, all single, double,... up to n-fold excitations, we can rewrite Eq. (3.81) as

$$R(\omega_x) = e^T |\mathbf{h}\rangle \mathbf{C}(\mathbf{C}^{-1} \left\langle \mathbf{h} \left| E_0 - \overline{H}_0 + \omega_x \right| \mathbf{h} \right\rangle^{-1} \tilde{\mathbf{C}}^{-1}) \tilde{\mathbf{C}} \langle \mathbf{h}| e^{-T} \quad (3.83)$$

$$= e^T |\mathbf{h}\rangle \left\langle \mathbf{h} \left| E_0 - \overline{H}_0 + \omega_x \right| \mathbf{h} \right\rangle^{-1} \langle\mathbf{h}| e^{-T} = e^T \mathbf{R}(\omega_x) e^{-T} \ ,$$

with

$$\mathbf{R}(\omega_x) = \left\langle \mathbf{h} \left| E_0 - \overline{H}_0 + \omega_x \right| \mathbf{h} \right\rangle^{-1} . \tag{3.84}$$

Hence, a convenient, perfectly general form for the frequency-dependent hyperpolarizabilities expressed in terms of unsymmetrical EOM-CC quantities is

$$X^n_{\alpha,\beta\ldots i} = \mathbf{P}_{\alpha,\beta,\ldots i} \langle 0|(1+\Lambda)\widetilde{\mu}_\alpha|\mathbf{h}\rangle \mathbf{R}(-\omega_\sigma)\langle \mathbf{h}|\widetilde{\mu}_\beta|\mathbf{h}\rangle \mathbf{R}(\omega_1 - \omega_\sigma)\langle \mathbf{h}|\widetilde{\mu}_\gamma|\mathbf{h}\rangle \tag{3.85}$$

$$\mathbf{R}(\omega_1 + \omega_2 - \omega_\sigma)\langle \mathbf{h}|\widetilde{\mu}_{i-1}|\mathbf{h}\rangle \mathbf{R}(-\omega_i)\langle \mathbf{h}|\widetilde{\mu}_i|\mathbf{0}\rangle , \tag{3.86}$$

where $\widetilde{\mu}_i = e^{-T}\overline{\mu}_i e^T - \langle \mu_i \rangle$, $\langle \mu_i \rangle = \left\langle 0 \left|(1+\Lambda)e^{-T}\mu_i e^T\right| 0 \right\rangle$.

The EOM-CC approach in its CI approximation offers a convenient recursive treatment of second and higher-order properties. We simply consider the usual perturbation expressions that can be used to define such frequency-dependent properties. Hence, all the frequency-dependent polarizabilities can be written as Eq. (3.86). over the configurations $|\mathbf{h}\rangle$. Since Eq. (3.86) is *exact*, it satisfies the time-reversal symmetry, and the *exact* form is independent of whether expectation values have the bra and ket states related as conjugates (see also [44]).

Since we use EOM-CCSD, the first approximation is to restrict $|\mathbf{h}\rangle$ to $|0, \mathbf{f_1 f_2}\rangle$, which introduces a lack of extensivity, as in any truncated CI approximation. But, it does not introduce any numerical time-reversal error even if it could for some approximations, as all computational expressions are built upon the average of frequency reversed expressions, as has been apparent from our first EOM-CC paper on polarizabilities [7], emphasized in refs [44] and [21], and is a customary expedient used, e.g. by Bishop [32]. Since including $|0\rangle$ in $|\mathbf{h}\rangle$ causes singularities for static properties, we also consider its exclusion, or alternatively an expansion in the *reduced* resolvent $R_0(\omega_x) = |\mathbf{f_1}, \mathbf{f_2}\rangle\langle \mathbf{f}|E_0 - \overline{H}_0 + \omega_x|\mathbf{f}\rangle^{-1}\langle \mathbf{f_1}, \mathbf{f_2}|$, which leads to renormalization terms. We also need to address the issue of renormalization terms. From consideration of the inverse, Eq. (3.84) can be readily expanded to

give the relation

$$R(\omega_x) = \omega_x^{-1} |0\rangle \langle 0| (1 + \Lambda) - |0\rangle \langle 0| (1 + \Lambda) R_0(\omega_x) + R_0(\omega_x) , \qquad (3.87)$$

where $R_0(\omega_x) = |\mathbf{f}\rangle \mathbf{R}_0(\omega_x) \langle \mathbf{f}|$. Substituting Eq. (3.87) into Eq. (3.82) we have

$$X^1_{\alpha\beta}(-\omega_\sigma, \omega_1) = \mathbf{P}_{\alpha\beta} \langle 0 | (1 + \Lambda) \widetilde{\mu}_\alpha R_0(\omega_1) \widetilde{\mu}_\beta | 0 \rangle \qquad (3.88)$$

since the other two terms must vanish by virtue of $\langle 0 | (1 + \Lambda) \widetilde{\mu}_\alpha | 0 \rangle = 0$. Then for the second- and third-order susceptibilities,

$$X^2_{\alpha\beta\gamma}(-\omega_\sigma; \omega_1, \omega_2) = \mathbf{P}_{\alpha\beta\gamma}[\langle 0 | (1 + \Lambda) \widetilde{\mu}_\alpha R_0(\omega_1 + \omega_2) \widetilde{\mu}_\beta R_0(\omega_2) \widetilde{\mu}_\gamma | 0 \rangle$$
$$- \langle 0 | (1 + \Lambda) \widetilde{\mu}_\alpha R_0(\omega_1 + \omega_2) \widetilde{\mu}_\beta | 0 \rangle \langle 0 | (1 + \Lambda) R_0(\omega_2) \widetilde{\mu}_\gamma | 0 \rangle]$$

$$(3.89)$$

$$X^3_{\alpha\beta\gamma\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) =$$
$$\mathbf{P}_{\alpha\beta\gamma\delta}[\langle 0 | (1 + \Lambda) \widetilde{\mu}_\alpha R_0(\omega_1 + \omega_2 + \omega_3) \widetilde{\mu}_\beta R_0(\omega_2 + \omega_3) \widetilde{\mu}_\gamma R_0(\omega_3) \widetilde{\mu_\delta} | 0 \rangle$$
$$- \langle 0 | (1 + \Lambda) \widetilde{\mu}_\alpha R_0(\omega_1 + \omega_2 + \omega_3) \widetilde{\mu}_\beta R_0(\omega_1) \widetilde{\mu}_\gamma | 0 \rangle \langle 0 | (1 + \Lambda) R_0(\omega_3) \widetilde{\mu_\delta} | 0 \rangle$$
$$- \langle 0 | (1 + \Lambda) \widetilde{\mu}_\alpha R_0(\omega_1 + \omega_2 + \omega_3) \widetilde{\mu}_\beta | 0 \rangle \langle 0 | (1 + \Lambda) R_0(\omega_1) \widetilde{\mu}_\gamma R_0(\omega_3) \widetilde{\mu_\delta} | 0 \rangle$$
$$- \langle 0 | (1 + \Lambda) \widetilde{\mu}_\alpha R_0(\omega_1 + \omega_2 + \omega_3) \widetilde{\mu}_\beta | 0 \rangle \langle 0 | (1 + \Lambda) \widetilde{\mu}_\gamma R_0(\omega_1) R_0(\omega_3) \widetilde{\mu_\delta} | 0 \rangle] .$$

$$(3.90)$$

which is a simple derivation of polarizability expressions without secular divergences [32]. The renormalization terms are exactly what one would expect from elementary considerations based upon inhomogeneous equations. For $\omega \neq 0$, an equally good computational procedure is to simply use Eq. (3.86) with $|\mathbf{h}\rangle = |0, \mathbf{f_1}, \mathbf{f_2}\rangle$ which avoids renormalization terms.

Once the configuration space is restricted the neglected higher excitations have two roles: to add additional correlation corrections, and, to cancel the unlinked

Table 3.1: Role of the renormalization terms at equilibrium geometries.

system / basis	$\beta(\|)^a$	$\beta(\|)^b$	$\beta(\|)^c$	$\beta(\|)^d$	$\gamma(\|)^a$	$\gamma(\|)^b$	$\gamma(\|)^c$	$\gamma(\|)^d$
HF/POL1	-5.44	-6.17	-5.76	**-6.08**	370	406	391	**403**
HF/POL1++	-7.10	-8.03	-7.67	**-7.89**	466	511	499	**504**
N_2/POL1	-	-	-	-	950	996	978	**991**
N_2/POL1++	-	-	-	-	990	1027	1009	**1024**
CO/POL1	23.0	24.5	23.8	**24.1**	1480	1519	1494	**1515**
H_2O/POL1	-12.1	-14.2	-13.4	**-13.9**	1210	1308	1269	**1278**
H_2O/POL1++	-14.9	-16.4	-15.4	**-16.0**	1710	1792	1744	**1768**
C_4H_6/ 6-31G+(P,D)	-	-	-	-	18480	20230	19610	**20030**

[a] finite field derivative of the orbital relaxed dipole moment
[b] EOM-CCSD analytical value without renormalization terms; EOM(1)
[c] EOM-CCSD analytical value with renormalization terms; EOM(2)
[d] finite field derivative of the EOM-CCSD quadratic polarizability (exact CCSD unrelaxed value)

diagrams (extensivity error) left in any truncated approximation. The second can be handled by including certain quadratic, cubic and quartic terms in $X^1_{\alpha\beta}$, $X^2_{\alpha\beta\gamma}$ and $X^3_{\alpha\beta\gamma\delta}$, respectively, which arise from coupled-cluster energy derivatives that correspond to certain higher-excitation effects [44, 46]. To regain the formally attractive perturbation theory form, which is only possible within configuration space, plus its convenient recursive generalization to any order, we prefer not to include the computationally difficult cubic and quartic terms, so we depend upon calibration to the available exact results in a given basis to offer confidence in the values. For static hyperpolarizabilities, such calibration is accomplished by comparing with finite field derivatives of the energy, dipole, or polarizability in the presence of a field. The procedure can also be used for the Kerr effect [47]. For other frequency-dependent results, we also compare to the known results [48]. All of these were employed to help justify our approximate results for the HF molecule. In Table 3.1, we show such an analysis.

Table 3.2: Percentage error of the EOM-CCSD static hyperpolarizabilities for $(LiH)_n$

R_{Li-H}= 1.59725 a.u., 3-21G basis set. All values in percent, unless noted otherwise.

number of LiH	$\beta(\|)^a$	$\beta(\|)^b$	$\beta(\|)^c$
1	1.2	0.6	**-501** a.u.
2	2.0	0.8	
3	3.1	1.1	
4	4.0	1.5	
5	5.4	1.9	
	$\gamma(\|)^a$	$\gamma(\|)^b$	$\gamma(\|)^c$
1	0.4	0.1	**78 580** a.u.
2	0.5	0.1	
3	0.6	0.1	
4	0.7	0.1	
5	0.7	0.1	

[a] EOM-CCSD CI-like without renormalization terms; EOM(1)
[b] EOM-CCSD CI-like with renormalization terms; EOM(2)
[c] finite field derivative of the dipole moment.

Neglecting the renormalization terms gives values which are actually closer to the exact values than if they are retained. Furthermore, the effect of orbital relaxation shown in the first column for β and γ, is far more numerically important than the differences in either of the EOM approximations, which, here, always bracket the exact value. It is evident, that either EOM approximation gives results within the estimated error bars of the calculations. For HF/POL1++ $\beta(\|)$ the orbital relaxation effect is -10%, while EOM(1)'s error is +1.8%, EOM(2) -2.8%, and the triples estimated effect is $\approx$ 5%.

We have also considered the problem of size extensivity of the resulting expressions (Table 3.2). Given a chain of non-interacting LiH molecules, in a 3-21G basis (all electrons), the percentage error for the first hyperpolarizability $\beta(\|)$ at $\omega = 0.0$, calculated using the unrenormalized EOM(1) method is 1.2% for one molecule and 5.4% for 5 molecules. The same errors computed with the EOM(2) approximation are 0.6% and 1.9% respectively. Percentage errors for the second

hyperpolarizability $\gamma(\|)$ at $\omega = 0.0$ are 0.4% and 0.7% for 1 and 5 LiH molecules in EOM(1) and 0.1% for both 1 and 5 LiH molecules in EOM(2).

Apparently, the renormalized EOM(2), which is generally in slightly poorer agreement with reference results, has a somewhat smaller extensivity error (although that does not mean it is closer to the complete CI limit). For *trans*-butadiene in the POL1++ basis, the differences between EOM(1) and EOM(2) for $\gamma(\|)$ are 0.72 at $\omega = 0.0$ a.u., 0.84 at $\omega = 0.0430$ a.u. and 1.18 at $\omega = 0.0656$ a.u. at the experimental geometry, compared to the estimated error bars of ± 2 a.u. in the calculations.

Since there is no orbital relaxation in the full CI limit, the remaining relaxation effect is partly indicative of how far from that limit the calculations remain.

3.2 Brillouin-Wigner Perturbation Theory Based Methods

In modern quantum chemistry of nondegenerate systems in which the ground state is well described by a single-determinant wavefunction, the Rayleigh-Schrödinger Perturbation Theory based methods (MBPT and CC) are very efficient for the description of properties. The most attractive feature of these methods is their size extensivity (proper scaling with the number of particles). Since size extensivity is a very important property of a method, it is expected that all the newly developed methods will satisfy this property. Possibly this is the reason why less attention has been paid to Brillouin-Wigner Perturbation Theory [49, 50, 51, 52]. Redefining λ in the perturbation expansion 3.4 gives us the opportunity to shape the form of the wavefunction and energy expansions. Choosing λ to be the total energy of the perturbed system E, we obtain the *Brillouin-Wigner* expansion, giving rise to BWPT. Putting $\lambda = E$ cancels $-E + \lambda$ in the resolvent expression 3.6 leads to

$$\Psi = \sum_{m=0}^{\infty} \left\{ \hat{R}_0(E)\hat{V} \right\}^m \Phi_0, \tag{3.91}$$

for the wavefunction and

$$\Delta E \ = \ \sum_{m=0}^{\infty} \langle \Phi_0 | \hat{V} \left\{ \hat{R}_0(E) \hat{V} \right\}^m | \Phi_0 \rangle. \tag{3.92}$$

for the energy expression.

The expansion in zero-order functions gives the following terms:

$$\left(\hat{H}_0 - E^{(0)} \right) | \Phi^{(1)} \rangle = \left(E^{(1)} - \hat{V} \right) | \Phi^{(0)} \rangle \quad \text{(first} - \text{order equation)}, \tag{3.93}$$

$$\left(\hat{H}_0 - E^{(0)} \right) | \Phi^{(2)} \rangle = \left(E^{(1)} - \hat{V} \right) | \Phi^{(1)} \rangle + E^{(2)} | \Phi^{(0)} \rangle \quad \text{(second} - \text{order)}, \tag{3.94}$$

$$\left(\hat{H}_0 - E^{(0)} \right) | \Phi^{(3)} \rangle = \left(E^{(1)} - \hat{V} \right) | \Phi^{(2)} \rangle \ + \ E^{(3)} | \Phi_0 \rangle + E^{(2)} | \Phi(1) \rangle$$

$$\text{(third} - \text{order)}, \tag{3.95}$$

$$\left(\hat{H}_0 - E^{(0)} \right) | \Phi^{(4)} \rangle = \quad \left(E^{(1)} - \hat{V} \right) | \Phi^{(3)} \rangle + E^{(4)} | \Phi_0 \rangle + E^{(3)} | \Phi(1) \rangle +$$

$$E^{(2)} | \Phi(2) \rangle \quad \text{(fourth} - \text{order)} \,. \tag{3.96}$$

After applying the left coupled-cluster ground state eigenvector and express the perturbed wavefunctions in terms of the zero order CC wavefunction we obtain

$$\langle \Phi_0 | \left(\hat{H}_0 - E^{(0)} \right) | \Phi^{(1)} \rangle = \langle \Phi_0 | \left(E^{(1)} - \hat{V} \right) | \Phi_0 \rangle \,, \tag{3.97}$$

$$\langle \Phi_0 | \left(\hat{H}_0 - E^{(0)} \right) | \Phi^{(2)} \rangle = \langle \Phi_0 | \left(E^{(1)} - \hat{V} \right) | \Phi^{(1)} \rangle + E^{(2)} | \Phi^{(0)} \rangle =$$

$$\langle \Phi_0 | \left(E^{(1)} - \hat{V} \right) R(E)_0 \hat{V} | \Phi_0 \rangle + E^{(2)} | \Phi_0 \rangle \,, \tag{3.98}$$

$$\langle \Phi_0 | \left(\hat{H}_0 - E^{(0)} \right) | \Phi^{(3)} \rangle = \langle \Phi_0 | \left(E^{(1)} - \hat{V} \right) | \Phi^{(2)} \rangle + E^{(3)} + E^{(2)} \langle \Phi_0 | \Phi^{(1)} \rangle$$

$$\langle \Phi_0 | \left(E^{(1)} - \hat{V} \right) R(E)_0 \hat{V} R(E)_0 \hat{V} | \Phi_0 \rangle + E^{(3)} + E^{(2)} \langle \Phi_0 | R(E)_0 \hat{V} | \Phi_0 \rangle \,,$$

$$\tag{3.99}$$

$$\langle \Phi_0 | \left(\hat{H}_0 - E^{(0)} \right) | \Phi^{(4)} \rangle = \langle \Phi_0 | \left(E^{(1)} - \hat{V} \right) | \Phi^{(3)} \rangle + E^{(3)} + E^{(2)} \langle \Phi_0 | \Phi^{(1)} \rangle =$$

$$\langle\Phi_0|\left(E^{(1)} - \hat{V}\right) R(E)_0 \hat{V} R(E)_0 \hat{V} R(E)_0 \hat{V}|\Phi_0\rangle + E^{(4)} + E^{(3)}\langle\Phi_0|R(E)_0\hat{V}|\Phi_0\rangle +$$

$$E^{(2)}\langle\Phi_0|R(E)_0\hat{V}R(E)_0\hat{V}|\Phi_0\rangle . \tag{3.100}$$

In above equations $R(E)_0$ is the BW resolvent operator

$$\begin{aligned}
R(E)_0 &= \sum_{ij} |\Phi_i\rangle\langle\Phi_i|E - \bar{H}_{ij}|\Phi_j\rangle\langle\Phi_j| \\
&= \sum_{ij} |\Phi_i\rangle\langle\Phi_i|E_0 - E^{(n)} - \bar{H}_{ij}|\Phi_j\rangle\langle\Phi_j|
\end{aligned} \tag{3.101}$$

defined for a non-diagonal $\bar{H}$ Hamiltonian.

The perturbed wavefunction $|\Phi(n)\rangle$ can be written in terms of the unperturbed ground state wavefunction with the excitation operators being actually perturbed:

$$|\Phi^{(1)}\rangle_{cc} = T^{(1)}|\Phi_0\rangle ,$$

$$|\Phi^{(2)}\rangle_{cc} = T^{(2)} + T^{(1)}T^{(1)}|\Phi_0\rangle ,$$

$$|\Phi^{(3)}\rangle_{cc} = T^{(3)} + T^{(2)}T^{(1)} + T^{(1)}T^{(1)}T^{(1)}|\Phi_0\rangle ,$$

$$|\Phi^{(4)}\rangle_{cc} = T^{(4)} + T^{(3)}T^{(1)} + T^{(2)}T^{(2)} + T^{(2)}T^{(1)}T^{(1)} + T^{(1)}T^{(1)}T^{(1)}T^{(1)}|\Phi_0\rangle .$$

$$\tag{3.102}$$

Applying the above results to the zero order expansions in Eqns. (3.93) to (3.96) and noting that $\langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right) T^{(n)}|\Phi_0\rangle = 0$ we get

$$E^{(1)} = \langle\Phi_0|\hat{V}|\Phi_0\rangle , \tag{3.103}$$

$$E^{(2)} = \langle\Phi_0|\left(E^{(1)} - \hat{V}\right) R(E)_0 \hat{V}|\Phi_0\rangle + \langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right) T^{(1)}T^{(1)}|\Phi_0\rangle , \tag{3.104}$$

$$\begin{aligned}
E^{(3)} &= \langle\Phi_0|\left(E^{(1)} - \hat{V}\right) R(E)_0 \hat{V} R(E)_0 \hat{V}|\Phi_0\rangle \\
&+ E^{(2)}\langle\Phi_0|R(E)_0\hat{V}|\Phi_0\rangle + \langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right) T^{(1)}T^{(1)}T^{(1)}|\Phi_0\rangle \\
&+ \langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right) T^{(2)}T^{(1)}|\Phi_0\rangle ,
\end{aligned} \tag{3.105}$$

$$E^{(4)} = \langle\Phi_0|\left(E^{(1)} - \hat{V}\right) R(E)_0 \hat{V} R(E)_0 \hat{V} R(E)_0 \hat{V}|\Phi_0\rangle$$

$$+ \quad E^{(3)}\langle\Phi_0|R(E)_0\hat{V}|\Phi_0\rangle + E^{(2)}\langle\Phi_0|R(E)_0\hat{V}R(E)_0\hat{V}|\Phi_0\rangle$$

$$+ \quad \langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right)T^{(1)}T^{(1)}T^{(1)}T^{(1)}|\Phi_0\rangle$$

$$+ \quad \langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right)T^{(2)}T^{(1)}T^{(1)}|\Phi_0\rangle$$

$$+ \quad \langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right)T^{(3)}T^{(1)}|\Phi_0\rangle$$

$$+ \quad \langle\Phi_0|\left(\hat{H}_0 - E^{(0)}\right)T^{(2)}T^{(2)}|\Phi_0\rangle . \tag{3.106}$$

In the same way as with the RSPT equations (3.27) to (3.29) we can derive expressions for static BW-EOM-CC polarizability and hyperpolarizabilities. Interestingly, the higher order terms coming from expanding $\Phi^{(n)}$ are exactly the same as in RSPT and they are completely independent on the choice of the resolvent and therefore time and frequency independent. Both this reason, the fact that the numerical significance of such expressions has been proven to be marginal [53] and difficulty and cost of computational implementation caused us to neglect these terms.

$$\alpha(0;0) = 2\langle 0|(1+\Lambda)\hat{V}R_0(\alpha)\hat{V}|0\rangle , \tag{3.107}$$

$$\beta(0;0,0) \quad = \quad 6\langle 0|(1+\Lambda)\hat{V}R_0(\beta)\hat{V}R_0(\beta)\hat{V}|0\rangle +$$
$$3\alpha(0;0)\langle 0|(1+\Lambda)R_0(\beta)\hat{V}|0\rangle ,$$

$$\tag{3.108}$$

$$\gamma(0;0,0,0) = 24\langle 0|(1+\Lambda)\hat{V}R_0(\gamma)\hat{V}R_0(\gamma)\hat{V}R_0(\gamma)\hat{V}|0\rangle +$$

$$3\beta(0;0,0)\langle 0|(1+\Lambda)R_0(\gamma)\hat{V}|0\rangle + 6\alpha(0;0)\langle 0|(1+\Lambda)R_0(\gamma)\hat{V}R_0(\gamma)\hat{V}|0\rangle .$$

$$\tag{3.109}$$

The equations (3.107) to (3.109) differ from similar RSPT equations by having fewer renormalization terms (had the Hamiltonian be symmetric and hermitian, no renormalization terms would be present in this approximation), by replacing the $\hat{W}$

operator by $\hat{V}$ (no extra unlinked terms coming from $-\langle 0|\hat{V}|0\rangle$) and by including the exact, unknown energy on both sides of the equation. The only plausible method of solving this type of equations is by iterating: the starting value of E (in most cases it is the second-order RSPT perturbed energy which is relatively easy to determine) the right hand side of Eqns. (3.107) to (3.109) is solved. The newly determined value of E is then inserted in the right hand side of these equations and the process is repeated until the value of E converges to desired accuracy. This feature, along with the slow convergence of the series and lack of size extensivity caused the BWPT method to be unpopular among quantum chemists, although it has been used extensively in nuclear physics [33]. In quantum chemistry the BWPT was first applied by Löwdin [54, 55, 56]. Related to this problem was the works of Brandäs and Bartlett [57, 58] and more recently by Hubač *et al* [59, 60, 61]. Thanks to the pioneering work of Hubač [61] we know that in the single-reference case, the BW theory based on the coupled-cluster wavefunction is fully equivalent to the standard CC theory and although the BWCC does not employ the Baker-Campbell-Hausdorff formula it is a fully size-extensive method since the iterative procedure used in solving the BWCC equations cancels out all disconnected diagrams (see Appendix 1). Because of the choice of our Hamiltonian, the right and left eigenvectors are not each other conjugates–they are biorthogonal. Thus, our left eigenvector expressed in terms of the ground state (Fermi vacuum) is $\langle \Phi_0| = \langle 0|(1+\Lambda)$ where Λ is a linear, CI-like deexcitation operator, complementary to the T excitation operator [42]. The right eigenstate is defined as $|\Phi_0\rangle = |0\rangle$.

Since the equations for static processes are readily extendible to evaluate the dynamic, frequency dependent quantities (as shown in Sect.3.1.1) and starting with the Fermi vacuum ground state, the final equations for (hyper)polarizabilities in the BWPT based EOM-CC are as follows:

$$\alpha_{ij}(-\omega;\omega) = \langle 0|(1+\Lambda)\left(E^{(1)} - \hat{V}_i\right) R(\omega,\alpha)\hat{V}_j|0\rangle$$

$$+ \quad \langle 0|(1+\Lambda)\left(E^{(1)} - \hat{V}_j\right)R(-\omega,\alpha)\hat{V}_i|0\rangle \qquad (3.110)$$

$$\beta_{ijk}(-\omega_\sigma;\omega_1,\omega_2) \;=\; P(i,\omega)\left(\langle 0|(1+\Lambda)\left(E^{(1)} - \hat{V}_i\right)R(\omega_\sigma,\beta)\hat{V}_j R(\omega_2,\beta)\hat{V}_k|0\rangle\right)$$

$$+ \quad P(i,\omega)\left(\alpha_{ij}(\omega_\sigma)\langle 0|(1+\Lambda)R(\omega_2,\beta)\hat{V}_k|0\rangle\right) \qquad (3.111)$$

$$\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) =$$

$$P(i,\omega)\left(\langle 0|(1+\Lambda)\left(E^{(1)} - \hat{V}_i\right)R(\omega_\sigma,\gamma)\hat{V}_j R(\omega_1+\omega_2,\gamma)\hat{V}_k R(\omega_1)\hat{V}_l|0\rangle\right)$$

$$+P(i,\omega)\left(\beta_{ijk}(\omega_3,\omega_2)\langle 0|(1+\Lambda)R(\omega_1,\gamma)\hat{V}_l|0\rangle\right)$$

$$+P(i,\omega)\left(\alpha_{ij}(-\omega_3)\langle 0|(1+\Lambda)R(\omega_2+\omega_1,\gamma)\hat{V}_k R(\omega_1,\gamma)\hat{V}_l|0\rangle\right) \qquad (3.112)$$

where ω_σ is a sum of all the incoming frequencies, $\omega_1, ..., \omega_n$ and $E^{(n)}$ is replaced by α, β, γ in the resolvent 3.101.

As mentioned earlier, the Brillouin-Wigner resolvent $R(E)$ is no longer secular at the excitation energy frequency: while the RSPT resolvent goes to 0 when the incoming radiation has the frequency corresponding to an internal electronic excitation ($\omega = E - H_0$), the BWPT resolvent remains finite due to a damping from the extra energy factor E_i (3.101). This enables us to study the nonlinear processes near and at the resonant frequencies in a fully consistent way.

The current progress in theoretical non-linear optics involves mostly non-resonant processes: there exist several models for calculation of hyperpolarizabilities, both optical, magnetic and magneto-optic. All of them however contain singularities at the poles of electronic excitations, making it impossible to determine the actual magnitude of a process at the resonance frequency. The divergence due to resonance is clearly unphysical, and ultimately has its origin in the neglect of higher-order terms and the quantum field interaction. When these are taken into account, large changes in the electron density caused by the resonance introduce level shifts. The general and widely accepted description of the non-linear effects is

based on the anharmonic oscillator model (Sum-Over-States expression) contains a damping factor in the denominator. This damping factor plays role of the level shifter here, but the actual choice of this quantity is based on empirical observations like natural lifetime in absence of collisions etc. This factor can be eventually obtained analytically by summation of the higher order terms [62].

Another way of a level-shifting technique is the Brillouin-Wigner perturbation expansion in which one has an exact energy on both sides of the SOS equation and the price paid for the flexibility of the method is that these equations have to be solved iteratively.

For more complicated properties with many different incoming and outgoing frequencies every denominator should in principle be the Brillouin-Wigner type level-shifted denominator. Since the energy shifts are also direction dependent (they are just the processes being computed), the convergence in such a case is very slow and the cost of such calculations is prohibitive.

A solution to this dillema is quite simple: because at any given frequency there can be only one resonant denominator, we can apply the BW level shifting to it and leave all the other denominators out of the iteration procedure, assigning them a standard shift (static value of the property in a given direction).

The numerical effect of such an approximation is expected to be very small as the leading, resonant term is much more significant numerically (typically 2-3 orders of magnitude) than the nonresonant terms. The example of these approximations is presented in Table 3.3. Here we compare the resonant linear polarizabilities of the HF molecule in the DZP polarized basis set.

The first polarizability is chosen for this example because the expression consists of only two terms and the explanation is rather straightforward. Obviously, the RS-EOM-CC method fails at the reonance due to the structure of its denominator (first column of the table). However, applying Eq.3.110 removes zero value

Table 3.3: Resonant linear polarizabilities of the HF molecule.

process/method	RS-EOM-CC	BW-EOM-CC[a]	BW-EOM-CC[b]
$\alpha_{zz}(+\omega)$	inf	2699.3	2695.8
$\alpha_{zz}(-\omega)$	1.1348	1.1348	1.1346

[a] Full form; from Eq. 3.110
[b] Approximated form; from Eq. 3.113

from the SOS denominator and delivers a reasonable value of the first polarizability (second column, BW-EO-MCC full). Of the two terms in Eq. 3.110 only one is at the resonance for either positive or negative value of the external electric field. Applying the full BW-EOM-CC expression is quite expensive computationally, as it requires 14 iterations to fully converge. However, if one substitutes the exact value of α in the non-resonant term by a constant (static polarizability value) and iterate the equation changing only the resonant term polarizability, the convergence is much faster. The resulting equation

$$
\begin{aligned}
\alpha_{zz}(-\omega;\omega) = \quad & \langle 0|(1+\Lambda)\left(E^{(1)} - \hat{V}_z\right) R(+\omega, \alpha(0))\hat{V}_z|0\rangle \\
& +\langle 0|(1+\Lambda)\left(E^{(1)} - \hat{V}_z\right) R(-\omega, \alpha(\omega))\hat{V}_z|0\rangle \quad (3.113)
\end{aligned}
$$

converges in 6 cycles and delivers almost the same value of the first polarizability.

For higher-order processes we may expect much higher computational cost in converging the BW-EOM-CC equations if all the frequency dependent moments are of the BW type.

CHAPTER 4
APPLICATIONS TO MOLECULAR SYSTEMS

4.1   First Polarizability and Long-Range Dispersion Coefficients

The working equation for EOM-CCSD polarizability has been already derived
(Eq. 3.79) and it reads

$$\alpha_{Aa}(\omega) = \sum_{l=0}^{1} \langle 0 | (1 + \Lambda) | \left(\bar{\mu}_A^{(0)} - \langle \bar{\mu}_A^{(0)} \rangle \right) | \mathbf{h} \rangle \mathbf{A}^{-1} \left((-1)^l \, \omega \right) \langle \mathbf{h} | \bar{\mu}_A^{(0)} | 0 \rangle \, , \qquad (4.1)$$

where $\mathbf{A}$ is defined as

$$\mathbf{A}(\pm\omega) = \langle \mathbf{h} | \left(\bar{H}^{(0)} - E^{(0)} \pm \omega \right) | \mathbf{h} \rangle \, . \qquad (4.2)$$

This provides a computationally and conceptually convenient alternative approach
to polarizabilities. The EOM-CC has the advantage of providing the $\Psi_k^{(0)}$, $\tilde{\Psi}_k^{(0)}$ and
$E_k^{(0)}$, $k = 0, 1, \dots$ in Eq. (3.78). From the above development it is clear that this
is not the full derivative for a truncated CC method, but it offers an equally valid
"propagator" viewpoint that has often been used in SOPPA and CCPPA property
calculations [63]. The analogy with an expectation value and the first-derivative of
the energy relative to a field is apparent. If the (generalized) Hellmann-Feynman
[64] theorem is satisfied, the two forms are identical. If not, different results are ob-
tained. Depending upon your viewpoint, either can be the "rigorous" definition of
the property. The same condition applies for second- and higher-order properties.
If the higher analogue of the Hellmann-Feynman theorem is satisfied, it means that
the results from ordinary perturbation theory and derivative theory are identical.
Since the derivative always introduces the appropriate non Hellmann-Feynman
terms, it should be somewhat superior numerically. The straight "propagator"
approach using the EOM-CC states is referred to as the CI-like approximation

[21], as the excited states in EOM-CC are obtained from a CI-like diagonalization procedure of a transformed Hamiltonian based upon a CC ground state. The EOM-CC approximation for excitation energies is not entirely linked [65], like CI. Second order properties in EOM-CC are fully linked in the quadratic approximation but not in the CI-like approach. This scarcely affects a single molecule, but if we replicate the molecule many times we would find a numerical problem with the CI-like approximation in the limit [66]. We can correct this, however, by removing the unlinked terms that remain in the CI-like approximation. Formally this means we take from the quadratic term that needed to correct the unlinked diagrams in the lead term, and then in the interest of efficiency, neglect the remaining linked quadratic part. This defines a linear linked approximation [67, 44]

$$\alpha_{Aa}(\omega) = \sum_{l=0}^{1} \langle 0| \, (1 + \Lambda') \, |\bar{\mu}_{A,open}^{(0)}|\mathbf{h}\rangle \mathbf{A}^{-}1((-1)^{l}\omega))\langle \mathbf{h}|\hat{\mu}_{a}^{(0)}|0\rangle \, . \qquad (4.3)$$

Here

$$\bar{\mu}_{A,open}^{(0)} = e^{-T}\mu_A e^{T} - \langle 0|e^{-T}\mu_A e^{T}|0\rangle \, ,$$

$$(4.4)$$

while Λ' is an explicitly connected operator that is defined from a slightly modified Λ equation obtained by equating the usually small matrix elements

$$\langle 0|e^{-T}He^{T}|_i^a\rangle = F_{ia} + \sum_{j,b} \langle ij||ab\rangle t_j^b \qquad (4.5)$$

responsible for disconnected contributions in Λ, rigorously to zero. The linear approximation scales properly for any number of molecules, but is no longer 'exact' for two electron systems. However, it retains the convenient "propagator" form, shared by the exact result. In practice we replace Λ' by Λ since this changes the results only very slightly, but it allows us to calculate both the CI-like and the linear approximations in a single calculation. It follows that in the present calculations,

if a molecule does not have a permanent dipole moment (due to symmetry) the linear and CI-like approximations yield identical results. In the next section we will also consider the fully linked linear approximation, and we will refer to this as linear' (in accordance with Λ'). Equations (3.76),(3.79) and (4.3) (with $\Lambda' = \Lambda$) summarizes the quadratic, CI-like and linear approximations to polarizabilities. In the following we will consider all three approximations numerically.

The difference between the CI-like and linear approximation to the polarizability can succintly be put as

$$
\begin{aligned}
\alpha_{Aa}\left(\omega\right)^{CI-like} \;=\;\; & \alpha_{Aa}\left(\omega\right)^{Linear} \\
& + \left(\langle 0|\bar{\mu}_A|0\rangle - \langle 0|\left(1+\Lambda\right)\bar{\mu}_A|0\rangle\right)\langle 0|\left(1+\Lambda\right)\cdot T_a\left(\omega\right)|0\rangle \\
& + \left(\langle 0|\bar{\mu}_a|0\rangle - \langle 0|\left(1+\Lambda\right)\bar{\mu}_a|0\rangle\right)\langle 0|\left(1+\Lambda\right)\cdot T_A\left(-\omega\right)|0\rangle \, .
\end{aligned}
$$

$$(4.6)$$

Therefore, in general, if the dipole moment of the reference determinant and the correlated CC dipole moment are similar, there is very little difference between the linear and CI-like approximations. For very large systems there is a problem with the CI-like approximation, however, because the term involving the perturbed amplitudes can grow indefinitely. For larger systems the linear approximation, therefore, offers distinct advantages over the CI-like approximation [67]. Most of our calculations are limited to small to medium sized systems and the difference between the linear and CI-like approximation due to improper scaling of the CI-like approximation is usually negligible. The other limiting case occurs when there is a large difference between the correlated and Hartree-Fock dipole moments. As an example we consider the HF molecule at three internuclear distances $R_0 = 1.7328$, 3.0 and 10.0 a.u. At the RHF level the system incorrectly separates into $H^+ + F^-$ fragments, and, correspondingly, carries a large dipole moment. The CCSD calculation brings this back to the proper ground state, separating into

neutral fragments, H + F, which in the limit does not have a dipole moment. This is ilustrated in table 4.1, where we list the dipole moments for the three distances considered. In table 4.1 we also include the t_1 CCSD amplitudes. These amplitudes are very large at larger separation indicating again that the Hartree-Fock reference state is not a good description of the true ground state. If we subsequently calculate the static polarizabilities we obtain the results presented in table 4.2. It is obvious that the CI-like and quadratic results agree quite well at all distances, but the linear version does not follow this pattern, and is in fact erroneous. Diagrammatic analysis shows that in the linear approximation, so-called EPV terms are neglected, and the present pathological example highlights these contributions. The situation is similar to the correlation energy. For two-electron systems CCSD and CISD are exact, and both can be said to include EPV terms. On the other hand, linearized CCSD does not include such contributions, but unlike CISD, it is rigorously size extensive. However, it is not exact for two-electron systems. In fact LCC(S)D usually overshoots the correlation energy. The situation for second order properties is a little different, because the extra (EPV-related) term in the CI-like approximation is usually very small. We have also included the fully linked linear' results. Compared to linear these results deviate further from the more correct quadratic results for larger separations. This can be understood because the disconnected contribution to Λ is quite appreciable (it follows the pattern for t_1^2), and in the linear' approximation we neglect such contributions from Λ, even though the *disconnected* contributions in Λ mainly give rise to *connected* contributions to the polarizability. In this context the extended coupled-cluster method (for analysis see ref. [64]), which treats both the right and left hand ground state in exponential fashion is most satisfactory.

Table 4.1: Dipole moments of the HF molecule.

R_{H-F} (a.u.)	μ (SCF)	μ (CCSD)	t_1 coefficients
1.7328 (R_e)	0.75628	0.70655	0.021
3.90	1.78678	0.58405	0.182
10.0	4.03577	-0.07291	0.396

Table 4.2: α_{zz} component of the static polarizability for the HF molecule.

R_{H-F} (a.u.)	CI-like	Linear	Linear'	Quadratic
1.7328 (R_e)	6.568	6.570	6.590	6.498
3.90	28.49	31.38	31.63	28.48
10.0	8.461	9.922	11.21	8.410

We conclude that in the single molecule calculations that are of practical interest to us, the CI-like approximation does not suffer significantly from the size-extensivity error. Due to the inclusion of EPV terms we actually expect it to be a little more accurate than the extensive linear approximation for some cases of interest. In all of the examples considered in this thesis (except the above pathological example) the CI-like and linear approximation yield identical results up to the figures quoted in this thesis. This is true exactly if molecules do not have a dipole moment due to symmetry. Let us emphasize finally that the EOM quadratic model as the derivative is formally most satisfactory, but it looses the convenient propagator form and can become expensive computationally. This is particularly true if we apply partitioning techniques to the EOM scheme [68, 69, 70]. We know this is a valid approach to polarizabilities as well as NMR spin-spin coupling constants [70], and in the partitioned model we definitely do not want to use the quadratic model, since it would forfeit all time-savings obtained by the partitioning.

In the following we wish to make a survey of several molecules in a consistent basis, rather tham the ulimate converged result for one example. Hence, we use experimental geometries and Sadlej's polarizability basis, POL1 [71, 72] which consist

of a (14s,10p,4d)/[7s,5p,2d] contraction for S, a (10s,6p,4d)/[5s,3p,2d] contraction for C, N and O and a (6s,4p)/[3s,2p] contraction for hydrogen. For trans-butadiene, to be consistent with prior work [5, 73],we have used the standard 6-31G basis set augmented by two diffuse p and d shells with the same exponent $\zeta_p = \zeta_d = 0.05$ which has been previously shown to combine small size with good accuracy for this molecule. Cartesian Gaussian basis functions have been used in all the calculations. All the results reported were obtained by using the ACES II program system [74].

The dipole polarizability is a diagonal second-rank tensor. For any linear molecule two of these three components are identical due to symmetry. The two unique components are commonly referred to as the perpendicular $\alpha_\perp$ and parallel $\alpha_\parallel$ components with respect to the principal rotational axis. The average polarizability $< \alpha >$ and the polarizability anisotropy $\Delta\alpha$ are the quantities most commonly determined experimentally [75]. They are defined as

$$
\begin{aligned}
< \alpha > &= \frac{\alpha(xx) + \alpha(yy) + \alpha(zz)}{3} \\
\Delta\alpha &= \frac{[(\alpha(xx) - \alpha(yy))^2 + (\alpha(xx) - \alpha(zz))^2 + (\alpha(yy) - \alpha(zz))^2]^{1/2}}{\sqrt{2}},
\end{aligned}
$$

$$(4.7)$$

which reduces to the simple expressions for molecules possessing a 3-fold or higher rotation axis (e.g. a linear molecule).

$$
< \alpha > = \frac{2\alpha_\perp + \alpha_\parallel}{3} \; ; \; \Delta\alpha = \left(\alpha_\parallel - \alpha_\perp\right) .
$$

$$(4.8)$$

All the molecules considered in this study are linear, and hence we report the average polarizability and the polarizability anisotropy (henceforth referred to as $< \alpha >$ and $\Delta\alpha$ respectively. The C_6 dispersion coefficients are calculated from

polarizabilities evaluated at selected imaginary frequencies $i\alpha$ using

$$C_6 = \frac{\pi}{3} \int_{-1}^{1} f(t)\, dt$$

(4.9)

and Gauss-Legendre quadrature where the function $f(t)$ is defined as

$$f(t) = \frac{2\omega_0}{(1+t)^2} \alpha \left(i\omega_0 \left[\frac{1-t}{1+t} \right] \right)$$

(4.10)

by means of the substitution

$$\omega = \omega_0 \left[\frac{1-t}{1+t} \right] .$$

(4.11)

The parameter ω_0 has been chosen to be 0.1 a.u. as in Amos *et al.* [76].

Nitrogen, Carbon Monoxide and Acetylene.

In tables 4.3,4.4 and 4.5 we present the calculated dipole polarizabilities of the N_2, CO and C_2H_2 molecules at several different frequencies along with the corresponding experimental results. The 'CCSD' results are obtained by the finite-field method as the difference of the analytically computed dipole moment [77] with orbital relaxation, and are limited to the static values. The TDHF values are from the analytical derivative program of Sekino and Bartlett [78]. For N_2 and CO we have also included second-order polarization propagator approximation (SOPPA) results [79], while for N_2, there are MC-TDHF results. Both the latter are in different basis sets from the CC results but agree exceptionally well with the EOM-CC results. As we can see from Tables 4.3 to 4.5, the electron correlation effects in general are fairly minor for these molecules, the TDHF and correlated dispersion for the isotropic component of the polarizability agrees fairly well for all methods. However, the most notable exception is the dispersion for $\Delta\alpha$ of the

CO molecule which is negative (but very small) at the TDHF level, and positive (but small) at the correlated level. This is likely to be related to the well-known sensitivity of the (small) dipole moment of CO which changes sign upon inclusion of correlation. In the case of acetylene the agreement is less satisfactory, even for the isotropic parts, while also the discrepancy between TDHF, SOPPA and the EOM models is more pronounced.

Orbital relaxation effects are very minor as follows from the comparison between finite-field-CCSD and the EOM-CC quadratic model for all three molecules. It is well known that CCSD shows remarkable insensitivity to orbital choice [80, 43], but the EOM-CCSD (or CCSD linear response) will not necessarily be as insensitive. Here, however, the ground state molecular orbital relaxation effects are very small. Finally the static, absolute, values for the CI-like and quadratic EOM-CC models agree quite nicely. Inclusion of correlation improves the agreement with experiment, but TDHF results are already pretty good.

Chlorine

The calculated dipole polarizabilities of the Cl_2 molecule for several different frequencies, and the corresponding experimental values are given in Table 4.6.

Here there is a substantial difference between the correlated dispersion and that given by TDHF. The EOM CI-like and quadratic model dispersion curves agree very well as before and there is only a minor effect from orbital relaxation. However, correlation effects for Cl_2 are more significant. For example, the correlation contribution to the static polarizability is 3.10 a.u. (10% of the total correlated (finite field CCSD) result) for $¡\alpha¿$ and 1.57 a.u. (0.94% of the total correlated result) for $\Delta\alpha$. The EOM-CCSD CI-like results overestimate the electron correlation effects by almost 1 a.u. compared to experiment, whereas the quadratic results lower the deviation to about 0.5 a.u. The role of correlation (and/or basis set)

Table 4.3: Dynamic polarizabilities of the N_2 molecule[a].

ω (a.u.)	TDHF[b]	SOPPA[c]	MCTDHF[h]	CCSD[b]	EOM-CCSD[b] CI-like	Quadratic	exp.
					$\langle\alpha(0)\rangle$		
0.0000	11.42	11.29	11.61	11.61	11.75	11.60	11.76[d]
					$\langle\alpha(\omega)\rangle - \langle\alpha(0)\rangle$		
0.0720	0.15	0.15	0.15		0.15	0.15	0.16[e]
0.0886	0.23	0.23	-		0.23	0.23	0.25[e]
0.0934	0.25	0.26	0.26		0.26	0.24	0.27[e]
0.0995	0.29	0.30	-		0.30	0.29	0.31[e]
					$\Delta\alpha(0)$		
0.0000	5.37	4.07	4.36	4.83	4.92	4.79	4.45[f]
					$\Delta\alpha(\omega) - \Delta\alpha(0)$		
0.0720	0.11	0.09			0.08	0.07	0.22[g]
0.0886	0.17	0.13			0.12	0.11	0.37[f]
0.0934	0.19	0.14			0.14	0.13	0.40[f]
0.0995	0.22	0.16			0.16	0.15	0.44[f]

[a] At the equilibrium experimental bond length r(NN) = 2.074 a.u. The $|\langle\epsilon\rangle|$ denotes the mean absolute deviation from experiment. This applies in all the following tables.
[b] The present work.
[c] Oddershede and Svendsen [79].
[d] Extrapolated from *International critical tables* [81].
[e] *International critical tables* [81].
[f] G. R. Alms *et al.* [82].
[g] Bridge and Buckingham [83].
[h] Luo and Jörgensen [84].

Table 4.4: Dynamic polarizabilities of the CO molecule[a].

ω (a.u.)	TDHF[b]	SOPPA[c]	CCSD[b]	EOM-CCSD[b]		
				CI-like	Quadratic	exp.
				$\langle \alpha(0) \rangle$		
.0000	12.23	12.45	12.95	13.28	13.07	13.08[e]
				$\langle \alpha(\omega) \rangle - \langle \alpha(0) \rangle$		
.0720	0.22	0.24		0.27	0.25	0.27[d]
.0886	0.34	0.37		0.41	0.39	0.41[d]
.0934	0.38	0.41		0.46	0.43	0.47[d]
.0995	0.44	0.47		0.52	0.50	0.66[d]
				$\Delta\alpha(0)$		
.0000	3.37	4.45	3.97	4.39	4.17	3.59
				$\Delta\alpha(\omega) - \Delta\alpha(0)$		
.0720	-0.01	0.07		0.03	0.02	3.59[f]
.0886	-0.01	0.10		0.03	0.03	-
.0934	-0.02	0.11		0.03	0.04	-
.0995	-0.02	0.12		0.04	0.04	-

[a] At the experimental equilibrium bond length R(CO) = 2.132 a.u.

[b] Present work

[c] Oddershede and Svendsen [79].

[d] *International critical tables* [81].

[e] Extrapolated from *International critical tables* [81].

[f] Bridge and Buckingham [83].

Table 4.5: Dynamic polarizabilities of the C_2H_2 molecule[a].

ω (a.u.)	TDHF[b]	CCSD[b]	EOM-CCSD[b] CI-like	Quadratic	exp.
			$\langle \alpha(0) \rangle$		
.0000	23.11	22.17	22.60	22.25	22.67^d
			$\langle \alpha(\omega) \rangle - \langle \alpha(0) \rangle$		
.0720	0.65		0.58	0.57	0.80^c
.0886	1.00		0.90	0.89	1.01^c
.0934	1.12		1.01	0.99	1.28^c
.0995	1.28		1.15	1.13	1.41^c
			$\Delta\alpha(0)$		
.0000	12.52	12.30	12.97	12.50	11.84^d
			$\Delta\alpha(\omega) - \Delta\alpha(0)$		
.0720	0.34		0.31	0.30	0.54^c
.0886	0.52		0.48	0.46	0.74^c
.0934	0.58		0.53	0.51	0.88^c
.0995	0.66		0.61	0.58	1.08^c

[a] The equilibrium experimental bond length r(CH) = 2.004 a.u. and r(CC) = 2.274 a.u.
[b] Present work.
[c] G. R. Alms*et al.* [82].
[d] Extrapolated from G. R. Alms *et al.* [82].

Table 4.6: Dynamic polarizabilities of the Cl_2 molecule[a].

ω (a.u.)	TDHF[b]	SOPPA[c]	CCSD[b]	EOM-CCSD[b]		
				CI-like	Quadratic	exp.
				$\langle \alpha(0) \rangle$		
.0000	27.38	24.42	30.48	31.32	30.86	30.35[e]
				$\langle \alpha(\omega) \rangle - \langle \alpha(0) \rangle$		
.0720	0.84	0.47		0.66	0.66	0.72[d]
.0886	1.31	0.74		1.04	1.03	1.11[d]
.0934	1.48	0.84		1.18	1.15	1.23[d]
.0995	1.70	0.98		1.37	1.32	1.41[e]
				$\Delta\alpha(0)$		
.0000	15.22	24.44	16.79	17.46	16.94	17.56[f]
				$\Delta\alpha(\omega) - \Delta\alpha(0)$		
.0720	0.95	0.86		0.58	0.56	-
.0886	1.50	1.29		0.91	0.85	-
.0934	1.69	1.43		1.04	0.95	-
.0995	1.96	1.60		1.20	1.07	-

[a] At the equilibrium experimental bond length r(ClCl) = 3.755 a.u.
[b] Present work.
[c] Oddershede and Svendsen [79].
[d] *International critical tables* [81].
[e] Extrapolated from *International critical tables* [81].
[f] Bridge and Buckingham [83].

effects is further demonstrated by the rather poor agreement of SOPPA results with the experimental values.

Carbon Dioxide, Carbon Oxysulfide and Carbon Disulfide.

In Tables 4.7 to 4.9 we present calculated $< \alpha >$ and $\Delta\alpha$ values for the CO_2, OCS and CS_2 molecules for several different frequencies. The results obtained by the TDHF method and experiment are also given for comparison.

It is evident from tables 4.7, 4.8 and 4.9 that orbital relaxation effects are very important for these molecules, and this importance increases with the number of sulfurs. The orbital relaxation effect (EOM quadratic - CCSD) for the isotropic

Table 4.7: Dynamic polarizabilities of the CO_2 molecule[a].

ω (a.u.)	TDHF[b]	CCSD[b]	EOM-CCSD[b]		
			CI-like	Quadratic	exp.
			$\langle \alpha(0) \rangle$		
.0000	15.84	17.44	18.47	18.00	17.52[c]
			$\langle \alpha(\omega) \rangle - \langle \alpha(0) \rangle$		
.0720	0.20		0.29	0.27	0.27[d]
.0886	0.30		0.44	0.42	0.34[c]
.0934	0.33		0.49	0.46	0.47[c]
.0995	0.38		0.56	0.53	0.50[c]
			$\Delta\alpha(0)$		
.0000	12.08	14.43	16.32	15.40	13.73[c]
			$\Delta\alpha(\omega) - \Delta\alpha(0)$		
.0720	0.26		0.41	0.40	0.54[d]
.0886	0.39		0.63	0.60	0.68[c]
.0934	0.44		0.71	0.68	0.88[c]
.0995	0.50		0.80	0.77	0.95[c]

[a] The experimental equlibrium bond length r(CO) = 2.195 a.u.
[b] Present work.
[c] G. R. Alms *et al.* [82].
[d] Extrapolated from G. R. Alms *et al.* [82].

60

Table 4.8: Dynamic polarizabilities of the OCS molecule[a].

ω (a.u.)	TDHF[b]	CCSD[b]	EOM-CCSD[b]		
			CI-like	Quadratic	exp.
			$\langle\alpha(0)\rangle$		
.0000	32.99	34.69	36.96	35.71	34.35[d]
			$\langle\alpha(\omega)\rangle - \langle\alpha(0)\rangle$		
.0720	0.90		1.13	1.09	0.67[c]
.0886	1.33		1.70	1.65	1.01[c]
.0934	1.56		1.91	1.86	1.21[c]
.0995	1.79		2.20	2.17	1.42[c]
			$\Delta\alpha(0)$		
.0000	24.01	27.55	32.50	29.97	26.25[d]
			$\Delta\alpha(\omega) - \Delta\alpha(0)$		
.0720	1.06		1.59	1.48	1.62[c]
.0886	1.57		2.42	2.29	2.57[c]
.0934	1.85		2.78	2.57	2.83[c]
.0995	2.12		3.19	2.97	3.11[c]

[a] The experimental bond length for R(OC) = 2.191 a.u. and R(CS) = 2.947 a.u.
[b] Present work.
[c] G. R. Alms et al. [82].
[d] Extrapolated from G. R. Alms et al. [82].

Table 4.9: Dynamic polarizabilities of the CS_2 molecule[a].

ω (a.u.)	TDHF[b]	CCSD[b]	EOM-CCSD[b]		
			CI-like	Quadratic	exp.
			$\langle \alpha(0) \rangle$		
.0000	55.18	55.03	62.10	59.15	55.40^d
			$\langle \alpha(\omega) \rangle - \langle \alpha(0) \rangle$		
.0720	2.50		2.84	2.89	3.24^c
.0886	3.93		4.67	4.62	5.27^c
.0934	4.42		6.49	5.25	5.94^c
.0995	5.10		7.47	6.05	6.82^c
			$\Delta\alpha(0)$		
.0000	56.58	56.50	73.74	66.51	58.71^d
			$\Delta\alpha(\omega) - \Delta\alpha(0)$		
.0720	5.03		6.27	6.24	6.41^c
.0886	7.97		10.34	10.01	10.66^c
.0934	9.00		12.38	11.33	12.28^c
.0995	10.44		14.41	13.19	14.31^c

[a] The equlibrium experimental bond length for R(CS) = 2.944 a.u.
[b] Present work.
[c] G. R. Alms $et\ al.$ [82].
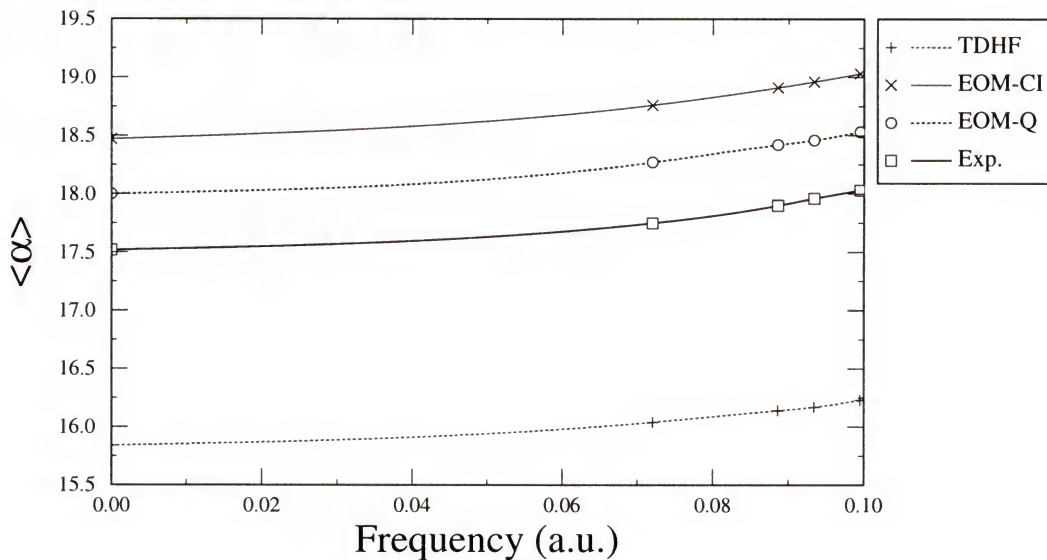[d] Extrapolated from G. R. Alms $et\ al.$ [82].

Figure 4.1: Mean dynamic polarizability of CO_2 in the POL1 basis set.

component increases as 0.6, 2.3 and 4.1 a.u in the series CO_2, OCS, CS_2, while for the anisotropic component this effect is enhanced from 1.0, 2.5 to 10.5 a.u. (!). Invariably, inclusion of orbital relaxation effects brings the results closer to experiment. Comparing the EOM CI-like and EOM quadratic models we find that the CI-like version overshoots the experimental results by up to 15 a.u. for the anisotropic component of CS_2. It is clear that for these molecules derivative techniques will work better than expectation-value based methods, but most of the error corresponds to orbital relaxation, which is not included in either method. Interestingly, the TDHF model performs better than the correlated EOM methods for these systems. Relaxation effects are, of course, precisely what is accounted for in TDHF. This, together with some unknown, but favorable, cancellation of errors is likely to account for the relative accuracy of the TDHF results. Of course, we also assume that the reference experimental values are reliable, even though in many cases these are rather old results.
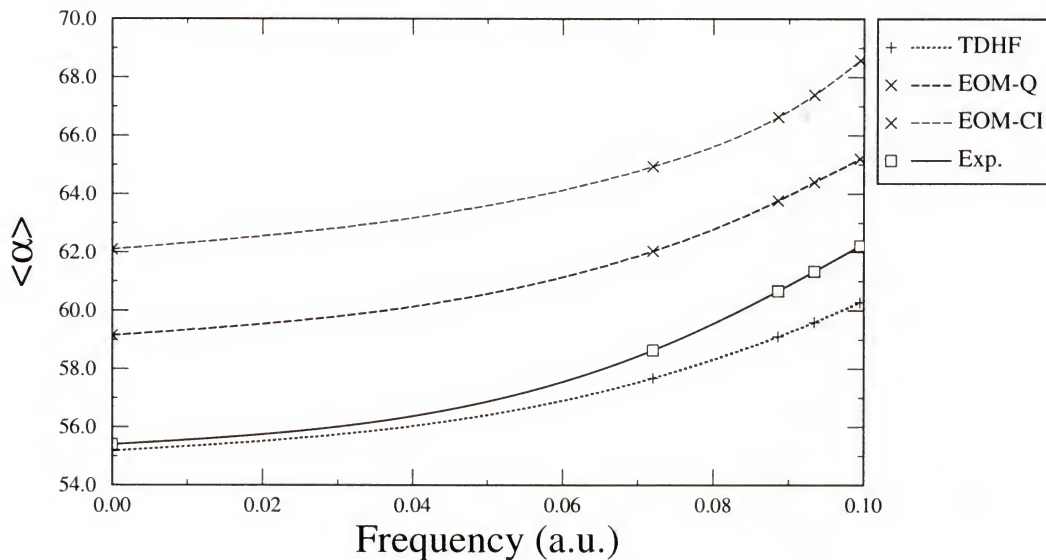
Figure 4.2: Mean dynamic polarizability of CS_2 in the POL1 basis set.

Dispersion effects in EOM-CC, on the other hand, are in reasonable agreement with experiment and greatly improve upon the Hartree-Fock dispersion curves. We note that the EOM CI-like model performs a little better that the EOM quadratic model compared to experiment, especially for higher frequencies.

From these comparisons we conclude, that if orbital relaxation effects appear to be important, they should be included. The potential importance of orbital relaxation in time-dependent properties is a tricky question. It is certainly possible to include orbital relaxation by building the correlated calculation on the underlying TDHF solution, just as coupled perturbed Hartree-Fock (CPHF) solutions are essential in analytical gradients and Hessian evaluations for the total energy. In that case orbital relaxation can never be neglected without invalidating the exactness of the critical points. The CCSD and higher methods, though, build in the vast majority of such relaxation effects via $|\phi'\rangle = e^{T_1}|\phi\rangle$ [33, 77], and such flexibility is usually sufficient for other kinds of properties [80]. However, when orbital relaxation is as large as found here for CS_2, we have to reconsider whether they should

be included in highly accurate calculations. However, to incorporate TDHF relaxation means also introducing artifactual TDHF (RPA) excitation energies (part of the propagator) into the calculation, which is unsatisfactory. Another obvious possibility is to include effects from connected triple and higher excitation operators in the calculation. Until the full CI is reached, though, there are still residual orbital relaxation effects. Here, apparently that effect is numerically significant. Interestingly the dispersion is, in all cases considered, well described by the CI-like model in EOM-CCSD. If we combine this with a finite field CCSD value for the static component (or full second order analytical CCSD derivative), we may expect to obtain reliable results, even when orbital relaxation effects are important.

Trans-butadiene

Table 4.10 shows the results of the dynamic polarizability calculation for the trans-butadiene molecule. Polyenes, of which trans-butadiene is a prototypical example are of substantial interest in NLO materials [85]. One can notice that TDHF values are much larger than the corresponding EOM values, due to the overestimation of the xx and yy components of α. The dispersion behavior is also very different: the percentage dispersion at $\omega = 0.0995$ a.u. is 10.3% of the TDHF level, 7.61% for the EOM CI-like method and 5.35% for the quadratic scheme. The quadratic correction accounts for up to 2-3% of the total correlation correction and also slightly changes the dispersion behavior: for the static case the difference between the CI-like and quadratic anisotropy is only 0.75 a.u. whereas for the largest computed frequency it amounts to 3.1 a.u. This result suggests that the dispersion of the dipole polarizability in conjugated hydrocarbons is sensitive to the correlation level. The fact that correlated results have been found to be further from experiment than TDHF [5, 73] has led to the argument [86] that for butadiene, and indeed linear polyenes in general, TDHF gives a better description of the hyperpolarizabilities than correlated methods. If so, the ultimate correlated

Table 4.10: Dynamic polarizabilities of the C_4H_6 molecule[a].

ω (a.u.)	TDHF[b]	CCSD[b]	EOM-CCSD[b]		exp.
			CI-like	Quadratic	
			$\langle \alpha(0) \rangle$		
.0000	52.04	48.79	49.78	49.16	58.31
			$\langle \alpha(\omega) \rangle - \langle \alpha(0) \rangle$		
.0720	2.58		1.87	1.16	
.0886	4.10		2.92	1.97	
.0934	4.63		3.32	2.26	
.0995	5.37		3.79	2.63	
			$\Delta\alpha(0)$		
.0000	50.29	35.24	36.26	35.51	
			$\Delta\alpha(\omega) - \Delta\alpha(0)$		
.0720	5.01		2.60	1.18	
.0886	8.06		4.13	2.20	
.0934	9.14		4.66	2.55	
.0995	10.67		5.41	3.02	

[a] The experimental equlibrium bond length $r(C_1 - C_2) = 2.508$ a.u. , $r(C_2 - C_3) = 2.768$ a.u., $r(C_1 - H_1) = 2.028$ a.u., $r(C_2 - H_3) = 2.035$a.u.
[b] Present work.
[c] [87]

methods must regain the TDHF results. However, it is difficult to see how the correlation effects can be neutralized. The extension of the atomic basis set and inclusion of vibrational effects must be considered.

Long-range London dispersion coefficients.

Table 4.11 lists the C_6 coefficients for the collection of atoms and molecules considered in this study. We use the same procedure previously discussed [88]. The largest errors are for CS_2 and OCS, consistent with our observation of the quality of the calculated polarizability results of the two respective molecules. Inclusion of the quadratic contribution improves the agreement of the calculated results with experiment and inclusion of orbital relaxation would presumably lead to still further improvements (see previous section).

There are several other correlated theoretical studies of C_6 coefficients of small molecules in the literature [89, 90, 88], the latter using EOM-CCSD. However, the only previous theoretical results of C_6 coefficients for CS_2 and COS are due to Spackman. The first column of Table 11 contains C_6 coefficients calculated by Spackman [91] at the TDHF level using a 6-31G basis set with added polarization functions. There are no previous theoretical or experimental C_6 coefficients for the Cl_2 molecule available in the literature.

Conclusions

The main focus of this chapter is to study the variation of the molecular polarizability with frequency (both real and imaginary) and to calculate the dispersion coefficients (C_6) for a series of molecules at a consistent level. For this purpose, we use the recently developed EOM-CCSD CI-like, linear and quadratic approximations to calculate frequency dependent polarizabilities of several selected small molecules. The EOM-CCSD CI-like approximation when combined with Sadlej polarized basis sets was shown previously to perform well for molecular dynamic polarizabilities [21]. In this thesis we also consider orbital relaxation effects on calculated static polarizabilities through finite difference CCSD calculations.

In general the difference between the EOM CI-like, linear and quadratic models is found to be minor, both for the net result and the dispersion. Also the results agree reasonably well with experiment. An important exception is the CS_2 molecule, and to a lesser extent OCS. In these cases we found orbital relaxation effects on the calculated static polarizabilities to be very important, implying significant potential effects on the dynamic polarizability. Even in these cases, however, the frequency dependence of the polarizabilities is well described at the EOM-CCSD level. If orbital relaxation is important a hybrid method like a combination of EOM-CCSD for dispersion and finite-field CCSD (or analytical CCSD second derivatives) for the static component could offer a pragmatic approach.

Table 4.11: C_6 dispersion coefficients for homonuclear interaction.

	TDHF[b]	EOM-CCSD (CI-like)[a]	EOM -CCSD (Quadratic)[a]	exp.
N_2	71.46	73.63	71.84	73.40^c
Cl_2	-	416.3	405.2	-
C_2H_2	196.6	204.3	196.9	231.4^d
CO	63.29	83.51	80.64	81.40^c
CO_2	123.1	173.6	166.4	158.7^c
SCO	368.5	453.1	481.4	402.2^c
CS_2	826.0	1182	1079	991.3^c

[a] Present work.
[b] M. A. Spackman [91].
[c] Margoliash and Meath [92] and M. A. Spackman [91].
[d] Starkschall and Gordon [93].
[e] Fowler *et al.* [94].

To better include orbital relaxation, in particular also the contribution to dispersion, the EOM-CCSD model can be extended with an approximate treatment for triples, like EOM-CCSDT-1 or EOM-CCSDT-3 [95]. Such triple contributions have been shown to introduce the most important remaining orbital relaxation terms [80]. The numerical effect of triple excitations (in cases that relaxation effects are not considered very important) on polarizabilities can be assessed from other results [77, 96], with the general conclusion that it increases the magnitude of the polarizability, but not necessarily the agreement with experiment.

Dispersion at the TDHF level is often a poor representation of the correlated EOM-CC dynamic polarizibility in the same basis set. Dispersion at the EOM-CCSD level agrees significantly better with the experimental measurements.

4.2 First and Second Hyperpolarizability

4.2.1 Hydrogen Fluoride

A number of papers have studied the hyperpolarizabilities of the FH molecule with correlation since 1979 [97, 98, 99, 100, 101, 102, 103, 85]. A critical analysis of all the high-level calculations until 1993 [101] concluded that, contrary to

several other molecules whose theoretical frequency-dependent hyperpolarizabilities agreed to within about 10% with gas phase experimental data, the theoretical results for FH showed an error of about 20%. Despite the small difference, and the very small magnitude of the FH hyperpolarizability that can enhance the percent error, high-level, correlated ab initio theory should be able to unambiguously provide agreement to within 10% for such a simple molecule, or the experimental value [104] should be reconsidered.

In prior theoretical work, the frequency dependence had been estimated from time-dependent Hartree-Fock (TDHF) theory [101], or from multiconfigurational linear response (MCLR) theory [100]. However, the former is uncorrelated and the latter includes mostly nondynamic correlation while much of the magnitude of hyperpolarizabilities arises from the large dynamic correlation effects. The latter are, perhaps, most accurately and conveniently included via coupled-cluster (CC) theory, but except for some Kerr effect studies [47], the prior CC results have not included the correlated frequency dependence that is consistent with CC theory. In this letter we have generalized the equation-of-motion (EOM-CC) method to recursively and analytically compute correlated, frequency dependent hyperpolarizabilities, to *any order*. This provides an unambiguous correlated measure for the dispersion effect. Furthermore, although many different kinds of basis sets have been considered which appeared to offer consistent results, there has not been a more systematic study based upon a series of n-aug-cc-pVXZ basis [105] to attempt to further eliminate this degree of uncertainty in the calculations. Here, we present such EOM-CC frequency-dependent results along with several other bases, to attempt to find basis set limit results.

The EOM-CC approach in its CI-like approximation [21, 53, 44] offers a convenient recursive treatment of second [21] and higher-order properties. We simply consider the usual perturbation expressions that can be used to define such

frequency-dependent properties. [1] Hence, all of the frequency-dependent polarizabilities can be written in the convenient form,

$$\chi^{(n)}_{i_1 i_2 .. i_n i_{n+1}} (\omega_\sigma; \omega_1, \omega_2, ..., \omega_n) = P(i_k \omega_k) \langle 0| (1+\Lambda) \bar{q}_{i_1} |\mathbf{h}\rangle \mathbf{R}(-\omega_1 - \omega_2 - ... - \omega_n)$$

$$* \langle \mathbf{h}| \tilde{q}_{i_2} |\mathbf{h}\rangle \mathbf{R}(-\omega_2 - \omega_3 - ... - \omega_n) * ... * \langle \mathbf{h}| \tilde{q}_{i_n} |\mathbf{h}\rangle \mathbf{R}(-\omega_n) \langle h| \tilde{q}_{i_{n+1}} |0\rangle$$

$$(4.12)$$

where $\mathbf{P}(i_k, \omega_k)$ denotes all the (n+1) permutations of the pairs $i_1 \omega_\sigma, i_2 \omega_1...$ and

$$\mathbf{R}(\omega_x) = \langle \mathbf{h}| E_0 - H_0 + \omega_x |\mathbf{h}\rangle^{-1} \qquad (4.13)$$

is the resolvent operator for the particular frequency ω_x. Also $\tilde{q}_i = \bar{q}_i - \langle \bar{q}_i \rangle$, where $\langle \bar{q}_i \rangle = \langle 0| (1+\Lambda) \bar{q}_i |0\rangle$ and $\bar{q}_i = e^{-T} q_i e^T$. Here, Λ is the deexcitation operator introduced previously [42] and q_i denotes the i-th component of the dipole moment vector. It should be clear from the above that, operationally, the repeated

---

[1] An alternative definition of second and higher order properties is offered for static ($\omega = 0$) cases by derivatives of the energy or the induced dipole moment. As is well known, even in the case of an expectation value versus the first derivative, the two definitions will not yield exactly the same results unless the Helman-Feynmann theorem is satisfied. For first-order properties in CC theory, this equivalence is ensured by virtue of the CC expectation value $< 0|(1+\Lambda)e^{-T}\Theta e^T|0 >$ for an operator Θ where both Λ and T are determined from stationary equations. However, the usual perturbation expansions for higher order properties are only strictly equivalent to higher derivatives when the higher-order analogues of the Helmann-Feynman theorem are satisfied, and this is not always the case [44]. The difference can be estimated from the numerical derivative value (unrelaxed) compared to the perturbation theory expression. Here that difference for the t-aug-cc-pVTZ basis is about 0.1 a.u. for $\beta_{||}(0)$ and $\gamma_{||}(0)$ so for all practical purposes for a single molecule there is no significant difference for this example. For other comparisons see [53, 106, 40]. This additional small effect is incorporated in the orbital relaxation estimates of this thesis. For the frequency dependent case, the perturbation theory definition can be immediately generalized by simply adding the appropriate non-zero ω to the resolvent [21] while the usual derivative approach is not directly applicable and requires some additional considerations [39, 53].

evaluation of the vectors

$$\mathbf{T}_{ij}^{(2)}\left(\omega_x\right) = \langle \mathbf{h}|\tilde{q}_j|\mathbf{h}\rangle T_i^{(1)}\left(\omega_x\right) \tag{4.14}$$

and

$$\mathbf{R}(\omega_y)T_{ij}^{(2)}\left(\omega_x\right) \tag{4.15}$$

where

$$\mathbf{T}_i^{(1)}\left(\omega_x\right) = R\left(\omega_x\right)\langle h|\tilde{q}_i|0\rangle \tag{4.16}$$

are the critical computational steps for *all* hyperpolarizabilites in the perturbation theory definition. This is actually accomplished by solving the corresponding linear equations of which the first is

$$\mathbf{R}^{-1}\left(\omega_x\right)T_i^{(1)} = \langle h|\tilde{q}_i|0\rangle \tag{4.17}$$

rather than taking the inverse of the resolvent [21]. Hence, there is no truncation of the excited states defined over the configurations $|\mathbf{h}\rangle$ as is often the case in sum over state approximations. Obviously, we can go to any order hyperpolarizability with the same program, just as was accomplished in the open ended TDHF method presented sometime back [3], making $\alpha, \beta, \gamma, \delta, \epsilon$ etc., readily accessible for whatever optical process, by virtue of using the correct form of $\mathbf{R}(\omega_x)$.

Using the above, numerical results in several bases are presented in Table 4.12. The modest J basis used previously consists of [6s5p5d1f] on F and [5s3p1d] on H and appears to be the best converged of our prior calculations [101]. The POL1 basis, due to Sadlej, is defined for polarizabilities [71]. Here we augment it with two additional shells of diffuse functions obtained by 0.3 times the most diffuse exponent of each in the POL1 basis to give [7s5p4d2f] on F and [5s4p1d] on H. The series of bases cc-pVTZ, aug-cc-pVTZ, d-aug-cc-pVTZ, t-aug-cc-pVTZ, q-aug-cc-pVTZ and p-aug-cc-pVTZ i.e. [9s8p7d6f/8s7p6d] with augmentation as considered

elsewhere [105] are hoped to provide a converging series. We also consider a t-aug-cc-pVQZ basis [8s7p6d5f4g/7s6p5d4f] to offer a different extension. Of course, as is usually the case for smaller bases, the FH $\beta_\parallel$ ($\beta_\parallel = 1/5 \sum_i (\beta_{iiz} + \beta_{zii} + \beta_{izi})$) tends to be too large, while adding further diffuse augmentation reduces the magnitude, which then eventually might grow, gradually, with basis set enhancement.

First, depending upon the n-augmented cc-pVTZ series, we would expect a second-harmonic generation (SHG) result of about -8.8 for a pentuply augmented cc-pVTZ basis, a result in line with the others shown. The larger values for $|\beta_{SHG}|$ correspond to probably excessive values for $|\beta_{zzz}|$, which is smaller in better basis sets. All of these results are at the EOM CCSD level and are still 20% in error compared to the center of the experimental value [100]. The dispersion correction given by EOM CCSD is 9.9%, in excellent agreement with the 9.6% estimate from TDHF that was previously used, and the 10% MCLR value. Hence, the prior dispersion estimates [101] were entirely justified for this problem , and did not introduce a significant error. We see a similar behavior for the direct-current induced second-harmonic generation process (γ_{dc-SHG}). Our J basis and extrapolated pentuply augmented result is 650 a.u., also 20% in error.

Besides dispersion and basis, there are several other items previously considered [101, 97, 98] to try to resolve the discrepancy between theory and experiment. These include the role of triple excitations as measured by static CCSD(T) results, vibrational averaging (i.e. r_e to r_0) in the ground state [98] , and the pure vibrational correction [107] that arises from vibronic intermediate states in perturbation theory expressions.

The magnitude of the triple excitations in CCSD(T) static values is -0.69 a.u. in the J basis [101], giving a CCSD(T) static value of $\beta_\parallel$ equal to -8.72 a.u.. In the t-aug-cc-pVTZ basis, CCSD(T) is -8.54 a.u. Using the latter triples effect (-0.62 a.u.), one would estimate a p-aug-cc-pVTZ CCSD(T) $\beta_\parallel(0)$ value of -8.57

Table 4.12: EOM-CCSD unnormalized static and dynamic ($\omega = 0.0656$ a.u. / 694.3 nm) hyperpolarizabilities of the HF molecule (in a.u.) at R_{HF}=1.7328 a.u., except where indicated.

	POL1++	J	d-aug-cc-pVTZ	t-aug-cc-pVTZ	q-aug-cc-pVTZ	p-aug-cc-pVTZ	t-aug-cc-pVQZ
$\beta_{zzz}(0)$	-10.60	-9.96	-9.87	-9.84	-9.85	-9.92	-9.83
$\beta_{zxx}(0)$	-1.39	-1.71	-1.53	-1.68	-1.70	-1.72	-1.74
$\beta_{\|}(0)$	-8.03	-8.03	-7.76	-7.92	-7.95	-7.95	-7.99
SHG[a]	-8.82	-8.85 (-9.18)^c	-8.52	-8.70 (-9.03)^c	-	-8.8^d	-
OR	-8.25	-8.22	-8.03	-8.22	-	-8.3^d	-
$\gamma_{zzzz}(0)$	340	367	369	378	-	-	-
$\gamma_{xxxx}(0)$	606	671	604	638	-	-	-
$\gamma_{xxzz}(0)$	150	178	163	178	-	-	-
$\gamma_{\|}(0)$	511	574	527	558	-	573^d	-
THG	665	741	669	711	-	735^d	-
dc-SHG[b]	564	650 (653)^c	588	629 (632)^c	-	650^d	-
δ_{zzzzzz}	-10 860	-13 520					
FHG$_{zzzzzz}$	-20 510	-24 850					

[a] Experimental value: -11 $\pm$ 1 a.u. [9]
[b] Experimental value: 840 $\pm$ 120 a.u. [9]
[c] r_0 values
[d] Estimated from extrapolation.

a.u. (Though the second decimal is certainly not significant in these estimates, we carry it temporarily for ease of analysis). Applying the same dispersion obtained in the EOM-CCSD calculations to the triples, we would obtain -9.61 a.u. in J and -9.48 a.u. for the estimated CCSD(T) SHG process in the p-aug-cc-pVTZ basis, assuming that there is no effect of the triple excitations on the dispersion. The computed pure vibrational correction is -0.35 a.u. [107] while -0.38 a.u. is the currently determined effect in the J or the t-aug-cc-pVTZ basis for evaluating EOM-CCSD β_{SHG} using formula (24) from [108] at four different internuclear distances[2] . Adding these to the EOM-CCSD SHG result gives -10.3 a.u. in J and -10.2 in the p-aug-cc-pVTZ basis, slightly within the error bars of the experiment. Why, then, is this different from all previous calculations [96] [3] which supported a maximum $|\beta_{SHG}|$ CCSD(T) result of -9.0, or -9.4, if the pure vibrational correction is included?

The principal difference between the present calculations and the prior ones is that in EOM-CC (or the related CCQR treatment of second- and higher-order properties [39] [4]), the orbitals are not allowed to relax to accommodate the perturbation, as they would be in a full derivative calculation. The important role

---

[2] This effect was previously found to be -0.28 to -0.37 a.u. [101], -0.48 [107], with the MCLR value being -0.62 [100]. The four values used in the J basis CCSD calculations of the SHG zero point average (using Bishop's formula [108]) are -8.53, -8.85, -9.18 and -9.52 a.u. for HF separation distances of 1.7026, 1.7328, 1.7620 and 1.7922 a.u. respectively.

[3] Shelton and Rice [102] cited unpublished CCSD(T) results in a large basis give $\beta_{||}(0)$=-7.31 a.u. $\gamma_{||}(0)$=525 a.u. These are nearly identical to the J basis result of [96], namely -7.43 a.u. and 525 a.u.

[4] A recent paper [40] reports SHG for HF using CCQR. In the same t-aug-ccPVTZ basis and frequency used here, the result is -8.789 a.u. The difference of 0.089 a.u. is a measure of the effect using the usual perturbation theory expression compared to the derivative expression.

of orbital relaxation for hyperpolarizabilities has been demonstrated previously [80]. This relaxation effect can be estimated by a finite field static calculation. This effect can be quite large as shown in Table 4.13. In the J Cartesian basis, the reduction in $\beta_{||}(0)$ is from -8.03 to -6.89(!). With the triples (whose relaxed value is -0.54 a.u.), we see how the best previous CCSD(T) $\beta_{||}(0)$ value of -7.4 a.u. arises. If we assume the same relaxation for the SHG process, our J basis result would be -7.71 which is close to the estimated CCSD J basis result before [101], and is more than 20% in error. Adding the above triples with estimated dispersion and vibrational corrections (i.e. -1.27 a.u.), our J basis SHG result would be -9.0 a.u., consistent with the best previous estimate. Doing the same exercise for the d-aug-cc-pVTZ, we obtain a relaxation effect of +0.52 in the spherical basis, giving a result of -9.3 a.u. If we also add the change due to the extra Cartesian components, assuming that in the absence of linear dependencies (none are found) the more functions, the better, we get a final extrapolated result of -9.1 a.u., quite close to that in the J basis. In the t-aug-cc-pVTZ case the Cartesian and relaxation effect is +0.55 a.u. (two linearly dependent functions are removed in the calculation). That makes the result become -9.4 a.u., still outside the error bars, but identical to the previous $|\beta_{SHG}|$ maximum of -9.4 a.u. The extrapolation to p-aug-cc-pVTZ gives -8.8 + (-1.3) = -10.1 a.u., while geometric extrapolation of the relaxation/Cartesian effect in the p-aug-cc-pVTZ basis suggests +0.3 a.u. to return to -9.8 a.u. still slightly outside the error bars, but better than the previous -9.4 a.u. estimate. Since we certainly believe that barring pathological situations, "relaxed" orbitals, are better than unrelaxed ones, and particularly for a property like hyperpolarizabilities that the more functions the better, which favors Cartesian bases over spherical ones; the best J, d-aug-cc-pVTZ and t-aug-cc-pVTZ results are consistent with all prior calculations, while the more extensive extrapolated

Table 4.13: CCSD and (CCSD(T)) orbital relaxation and basis set effects (in a.u.) in the β and γ static hyperpolarizabilities of HF

Basis	Relaxed orbitals		Unrelaxed orbitals	
	Spherical	Cartesian	Spherical	Cartesian
j				
$\beta_\parallel$	-7.50	-6.89 (-7.60)	-8.06	-8.03 (-8.72)
$\gamma_\parallel$	-	478 (526)	-	574 (631)
d-aug-cc-pVTZ				
$\beta_\parallel$	-7.24	-7.07	-7.76	-7.63
$\gamma_\parallel$	(538)	-	(591)	-
t-aug-cc-pVTZ				
$\beta_\parallel$	-7.51	-7.37	-7.92	-7.84
$\gamma_\parallel$	530 (582)	539	558 (613)	571
q-aug-cc-pVTZ				
$\beta_\parallel$	-7.60 (-7.87)	-	-7.95 (8.19)	-

p-aug-cc-pVTZ result suggests some improvement to -9.8 a.u. Even the use of the very large t-aug-cc-pVQZ basis does not change this result.

We can make the same type of estimate for the experimentally known dc-SHG process for γ. The previous theoretical results (with exclusion of the pure vibrational correction) were estimated to show a value of 660±60 a.u. [101] compared to 840±120, experimentally.

The best of the new EOM-CCSD results, including the extrapolated p-aug-cc-pVTZ and previously used J basis are 650 a.u. The EOM-CCSD dispersion effect for dc-SHG is 12.7% in the t-aug-cc-pVTZ basis compared to TDHF value of 12.5% and much higher MCLR value of 19% [100]. For γ_{dc-SHG}, we can estimate the contributions from triples corrections, vibrational averaging and the pure vibrational part from our current work and from [107]. In the J basis triples corrections amount to 57 a.u. plus 8 a.u. for dispersion (65 a.u.). Adding the pure vibrational correction of -5.5 a.u. from [107], and 3 a.u. computed by changing r_e to r_0, without orbital relaxation, we get 62 a.u. added to the γ_{dc-SHG} EOM-CCSD

result, to give 712 a.u. as the estimated CCSD(T) γ_{dc-SHG} in the J basis, just outside the experimental error bars. If we include the very large static CCSD(T) relaxation (-105 a.u.) in the J basis, we get 607 a.u., well outside the error bars. In the d-aug-cc-pVTZ basis the relaxation is reduced to 53 a.u. In the t-aug-cc-pVTZ basis, the effect of triples is 55 a.u. plus dispersion (62 a.u.), but the relaxation effect is only -31 a.u., giving 663 a.u. The Cartesian components would appear to add 9 a.u. plus - 5.5 a.u. for the pure vibrations to give 667 a.u. Finally, the estimated p-aug-cc-pVTZ CCSD(T) dc-SHG (extrapolation of relaxation effect suggests 10 a.u.) gives a nearly identical 666 a.u., again well outside the error bars. Despite the best efforts from 18 years of quantum chemistry, it would appear that there is still some disagreement between theory and experiment for β_{SHG} and γ_{dc-SHG} for the FH molecule. The best current theoretical results for γ_{dc-SHG} and β_{SHG} do not quite fall within the rather generous error bars. If orbital relaxation could be neglected, agreement would be achieved even in modest basis sets. In a complete basis, of course, there is no relaxation effect, but other than that, there are two arguments for dismissing orbital relaxation, one practical and one formal. Practically, when using an RHF reference in a correlated calculation, at large bond lengths, relaxed RHF orbitals have the wrong behavior, since RHF goes to an ionic separated atom limit, which the correlated method is attempting to undo. However at equilibrium, even for a fairly ionic molecule like HF, one would not believe that unrelaxed orbitals are closer to the truth than relaxed orbitals. The formal objection is that inclusion of Hartree-Fock orbital relaxation introduces artificial excitation energy poles in the dynamic polarizability, in addition to the correct ones [109]

However, it is absolutely necessary to use relaxed orbitals in gradient and hessian calculations, as the critical point would not be well defined otherwise. Why should it be different for other kinds of properties? The orbital relaxation terms

introduced by adjusting the orbitals in the presence of the perturbation would correspond to an infinite sum of diagrams if they were introduced via evaluation in terms of the unrelaxed orbitals [110, 80]. CCSD easily sums many of these diagrams [80], (CCSDT sums more) but not all. For many properties, the infinite sums inherent in CC makes orbital choice largely irrelevant [111], but apparently not for the hyperpolarizabilities of FH, at least at the CCSD(T) level, as this subtle effect accounts for the current and previously observed differences between theory and experiment. In a complete basis, relaxation is irrelevant, but we do not seem to approach that in the current calculations, even in the p-aug-cc-pVTZ basis. For the more common applications to polyatomic molecules, it is even less likely, and it would appear orbital relaxation should not be neglected in rigorously computed answers. Here, our best final, "relaxed" results are -9.8 a.u. for β_{SHG} and 670 a.u. for γ_{dc-SHG}. Considering the estimates made, a $\pm$ 5% error would probably be justified in each (-9.8 $\pm$ 0.5 a.u. and 670 $\pm$ 40 a.u.), causing the experimental and theoretical error bars to overlap. However, the center of the experiment and theoretical calculation remains about 11% apart for β_{SHG} and 19% for γ_{dc-SHG}. If orbital relaxation could be neglected, our best results would be -10.2 $\pm$ 0.5 a.u. and 700 $\pm$ 40 a.u. compared to -11 $\pm$ 1 and 840 $\pm$ 120, experimentally.

4.2.2 *trans*-Butadiene

Trans-butadiene has served for many years as the prototype system for polyenes which have attractive intrinsic nonlinear optical properties (NLO). Clearly, if quantum chemistry is to play a role in the design of NLO materials, it must be able to correctly account for butadiene's hyperpolarizability.

However, it has been pointed out in several papers [5, 47, 85] that trans-butadiene's theoretically determined hyperpolarizability behaves differently compared to several other molecules [101, 85]. Whereas for N_2, CO, CO_2, H_2, HF,

HCl, NH_3, H_2O and others, correlation effects evaluated with MBPT or CC theory provides substantial improvement compared to experiment [101, 85], as they should, for butadiene correlation appears to hurt the agreement, as the uncorrelated TDHF value for $\gamma_{||}$ for butadiene (and to a lesser extent ethylene) appears to give very good agreement with experiment while MBPT(2) and CCSD appears to change this value dramatically [5, 47]. Furthermore, recently, Norman *et al.* [112] made the statement with reference to TDHF that "... none of the more sophisticated correlating methods are able to match this accuracy...," implying that TDHF applied to dynamic hyperpolarizabilities of *trans*-butadiene and other linear polyenes provide accuracy exceeding that of highly-correlated coupled-cluster methods.

The history of quantum chemistry is checkered by many examples of excellent, but accidental agreement between theory and experiment, largely based on fortuitous cancellation of errors. If TDHF "gets the right answer for the right reason," then all correlation effects must effectively vanish, which seems highly unlikely. To answer this question, a more detailed study is necessary, taking into consideration basis set effects, vibrational corrections, higher excitation contributions and molecular geometry. Although it has been possible to do MBPT and coupled-cluster calculations of static hyperpolarizabilities for a long time [97, 5, 101], a consistent approach to dynamic processes has not been possible until recently [47, 48, 40]. We can now calculate frequency dependent hyperpolarizabilities for any order and any process, recursively, using the EOM-CCSD method [37, 68, 20, 21]. Hence, we are now in a position to offer more definitive correlated results.

The average hyperpolarizability of *trans*-butadiene in C_{2h} symmetry for the dc-SHG process is defined as

$$\gamma_{||}\left(-2\omega;\omega,\omega,0\right) =$$

$$\frac{1}{5}\left(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + \gamma_{xxyy} + \gamma_{yyxx} + \gamma_{xxzz} + \gamma_{zzxx} + \gamma_{yyzz} + \gamma_{zzyy}\right)$$

$$(4.18)$$

The actual working equation for a single component of the dc-SHG process is quite simple when based upon the standard perturbation expression [21, 48]:

$$
\begin{aligned}
\gamma_{zzzz}\left(-2\omega; \omega, \omega, 0\right) \quad &= P\left(\omega\right)\left[\langle 0|\left(1+\Lambda\right)\tilde{q}_z R\left(-2\omega\right)\tilde{q}_z R\left(-\omega\right)\tilde{q}_z R\left(0\right)\bar{q}_z|0\rangle - \right.\\
&\quad \langle 0|\left(1+\Lambda\right)\tilde{q}_z R\left(-2\omega\right)\bar{q}_z|0\rangle\langle 0|\left(1+\Lambda\right)R\left(-\omega\right)\tilde{q}_z R\left(\omega\right)\bar{q}_z|0\rangle - \\
&\quad \left.\langle 0|\left(1+\Lambda\right)\tilde{q}_z R\left(-2\omega\right)\bar{q}_z|0\rangle\langle 0|\left(1+\Lambda\right)\tilde{q}_z R\left(-\omega\right)R\left(\omega\right)\bar{q}_z|0\rangle\right]
\end{aligned}
$$

$$(4.19)$$

where the permutation operator P(ω) permutes the frequencies $(-2\omega, \omega, \omega, 0)$ with their associated spatial subscripts (here: z,z,z,z). Similarly, we can readily evaluate the THG, IDRI and EOKE processes. In the above expression $R_0(n\omega)$ is a frequency-dependent resolvent:

$$R\left(\pm n\omega\right) = |\mathbf{h}\rangle\langle\mathbf{h}|E_{cc} - \bar{H}_0 \pm n\omega|\mathbf{h}\rangle^{-1}\langle\mathbf{h}| \qquad (4.20)$$

In our current calculations we employ three sets of basis functions: that previously used in *trans*-butadiene calculations [113, 5, 47] 6-31G+(P,D) basis [3s3p1d/2s], obtained by augmenting the standard 6-31G set by one p and one d gaussian with the exponent ζ=0.05, the standard POL1 set [71] [5s3p2d/3s2p] and finally, the doubly augmented POL1 set [5s4p3d1f/5s4p1d], denoted POL1++ [48] here. The geometry plays an important role in these calculations, especially the TDHF ones. We choose the three sets of coordinates in Table 4.14: that obtained by the SCF optimization in 6-31G basis (geometry I) previously used, that obtained by a CCSD optimization in the 6-31G+(P,D) basis (geometry II), and the "experimental" geometry from Haugen and Traetteberg [114].

Table 4.14: Geometry of the *trans*-butadiene molecule at various levels of optimization

Variable	SCF (I)	CCSD (II)	exp^a (III)
C_2-C_3	1.465Å	1.481Å	1.467Å
C_1-C_2 = C_3-C_4	1.327Å	1.361Å	1.343Å
C_1-C_2-C_3	124.3°	124.0°	122.8°

[a] Ref. [114]

In the small basis set originally used, 6-31G+(P,D) [5, 47] the static EOM-CC averaged hyperpolarizability is 19.61 (here we assume the units of 10^3 a.u.), whereas the corresponding SCF result is 13.62. Our previous studies [48] show a large effect of including the Cartesian component of the d shell in smaller basis sets. Introducing this component the EOM-CC and SCF hyperpolarizabilities are 20.17 and 14.81, respectively.

The essence of the controversy is that for dc-SHG the TDHF results in the 6-31G+(P,D) Cartesian basis, at ω=0.0430 a.u. and ω=0.0656 a.u. are 18.2 and 24.9, which are in reasonable agreement with experiment (20.2 and 27.7 respectively). The above static MBPT(2) correlated results in this basis augmented by the percentage TDHF dispersion to estimate the correlated dc-SHG results, were substantially in error at 25.3 and 34.8 respectively [5]. Of course, there are many potential sources of error in such a calculation, particularly the dispersion estimates, and a different estimate of the dispersion [47], based upon the relation of Bishop [115], plus CCSD instead of MBPT(2), reduced the correlated value to 24.3 and 29.7, in better agreement with experiment. However, neither of these results is satisfactory, as the proper result comes from a correlated, frequency dependent calculation. In order to obtain a more definitive result, we consider much larger basis sets and geometry effects, as well as the correlated frequency dependence.

Table 4.15 presents 6-31G+(P,D) TDHF and EOM-CCSD frequency dependent hyperpolarizabilities in the three different basis sets at geometry I. Since the POL1

Table 4.15: Static and dynamic hyperpolarizabilities of *trans*-butadiene (in 10^3 a.u.) in geometry I.

In parentheses, values obtained with all 6 Cartesian components of the d shell.

		THG	dc-SHG	IDRI	EOKE
	TDHF				
0.0000	6-31G+(P,D)	13.62(14.81)	13.62(14.81)	13.62(14.81)	13.62(14.81)
	POL1	*13.92*	*13.92*	*13.92*	*13.92*
	POL1++	13.70	13.70	13.70	13.70
0.0430	6-31G+(P,D)	20.78(22.96)	16.53(18.2)	15.45(16.89)	14.49(15.80)
	POL1	22.33	17.29	16.02	14.91
	POL1++	22.37	17.14	15.84	14.71
	exp		**20.18**[a]		
0.0656	6-31G+(P,D)	55.21(62.58)	22.46(24.93)	18.55(20.47)	15.80(17.28)
	POL1	*64.49*	*24.44*	*19.73*	*16.42*
	POL1++	74.50	24.60	19.67	16.25
	exp		**27.70**[a]		
0.0882	6-31G+(P,D)	35.87	40.92	25.03	18.02
	POL1	*140.14*	*49.24*	*28.14*	*19.03*
	POL1++	40.72	51.67	28.59	18.94
	EOM-CC				
0.0000	6-31G+(P,D)	19.61	19.61	19.61	19.61
	POL1	*17.32*	*17.32*	*17.32*	*17.32*
	POL1++	18.17	18.17	18.17	18.17
0.0430	6-31G+(P,D)	27.00	22.59	22.00	20.74
	POL1	*39.27*	*20.57*	*19.55*	*19.11*
	POL1++	36.74	22.45	20.56	19.29
	exp		**20.18**[a]		
0.0656	6-31G+(P,D)	40.81	29.19	26.22	22.51
	POL1	*36.46*	*26.63*	*23.32*	*20.77*
	POL1++	39.31	27.76	24.57	20.99
	exp		**27.70**[a]		
0.0882	6-31G+(P,D)	93.63	43.68	33.24	26.27
	POL1	*101.31*	*36.82*	*29.48*	*23.04*
	POL1++	104.40	45.50	31.35	24.76

[a] Ref. Shelton and Rice [116], Ward and Elliott [117]

Table 4.16: Static and dynamic hyperpolarizabilities of *trans*-butadiene (in 10^3 a.u.) in geometry II.

Upper row: TDHF values. Lower row: EOM-CCSD values

process	6-31G+(P,D)	POL1	POL1++	exp^a
static, $\omega = 0$	16.42 *18.43*	15.46 *17.19*	15.29 *18.06*	-
dc-SHG, $\omega = 0.0430$	20.41 *22.04*	19.54 *20.95*	19.47 *21.18*	20.18±0.11
dc-SHG, $\omega = 0.0656$	29.01 *29.73*	28.66 *28.61*	29.04 *29.56*	27.70±1.60

[a] Ref. Shelton and Rice [116], Ward and Elliott [117]

and POL1++ sets do not show such large differences, we limit ourselves to the spherical components only. For TDHF the 6-31G+(P,D) results always lie below the experimental values and it appears that the POL1++ basis is converged since the difference between POL1 and POL1++ is always quite small. On the other hand, the EOM values tend to oscillate with a minimum at the POL1 values.

In order to assess the geometry effect the dc-SHG values given in Table 4.15 for geometry I may be compared with those for geometries II and III given in Tables 4.16 and 4.17 respectively. (The TDHF values of $\gamma(0)$ in the 6-31G+(P,D) basis have a quite large range: from 14.81 at the SCF optimized geometry to 16.42 at the CCSD geometry.) The EOM results vary very little with geometry being 18.9 ± 0.5. As the basis size increases from POL1 to POL1++, the TDHF static hyperpolarizabilities appear to be well converged, while EOM results increase by almost 5% in all geometries. Our EOM-CCSD values of $\gamma(0)$ in the POL1 basis are close to those obtained by finite differentiation of the CCSD energy by Kirtman *et al.* [118]. Our results of 17.32, 17.19 and 17.24 in geometries

Table 4.17: Second hyperpolarizabilities of *trans*-butadiene at the experimental geometry (III).

Upper row: TDHF values. Lower row: EOM-CCSD values

process	6-31G+(P,D)	POL1	POL1++	exp^a
static, $\omega = 0$	16.09 *18.60*	14.62 *17.24*	14.52 *18.13*	-
dc-SHG, $\omega = 0.0430$	20.00 *22.09*	18.33 *20.26*	18.28 *21.27*	20.18±0.11
dc-SHG, $\omega = 0.0656$	28.42 *30.23*	26.42 *27.96*	27.54 *29.63*	27.70±1.60

[a] Ref. Shelton and Rice [116], Ward and Elliott [117]

I,II and III, respectively, are close to the value of 18.0 obtained therein. Hence, these numbers show little effect of the non-Hellmann-Feynman terms, that are due to orbital and additional CC amplitude response [44], that are excluded here, but would be included in the numerical derivatives as discussed elsewhere [48]. Table 4.15 contains the values for four fourth-order processes: third-harmonic generation (THG) $\gamma(-3\omega;\omega,\omega,\omega)$, dc induced second-harmonic generation (dc-SHG) $\gamma(-2\omega;\omega,\omega,0)$, intensity dependent refractive index (IDRI) $\gamma(-\omega;\omega,-\omega,\omega)$ and the electro-optic kerr effect (EOKE) $\gamma(-\omega;\omega,0,0)$. The dc induced optical rectification (dcOR) $\gamma(0;\omega,-\omega,0)$ after averaging is the same as EOKE so it will not be considered separately.

For 1,3-*trans*-butadiene the experimental values have been determined only for the dc-SHG process [116], [117] by the dc electric-field induced optical SHG experiment. The effect at the ruby-laser frequency (0.0656 a.u.) is 27.7 ± 1.6 while at 0.0430 a.u. it is 20.2 ± 0.1. In the SCF optimized geometry (Table 4.15) the TDHF values are consistently ca. 3 units too small compared to experiment, while EOM values are larger by about 1 to 3 units. At the CCSD and experimental geometry

the EOM values for dc-SHG are systematically larger than experiment whereas the TDHF values may be either larger or smaller. Moving from the 6-31G+(P,D) basis to POL1 generally improves the EOM results. Adding extra functions to the POL1 basis increases the EOM-CCSD results by 1 to 2 units. For trans-butadiene, the only previous correlated frequency dependent hyperpolarizability calculation was evaluated by finite field differentiation of the frequency dependent linear polarizability [47] to give values for the Electro-Optic Kerr Effect (EOKE): they are 20.7, 21.9 and 23.7 at frequencies $\omega=0.0$, $\omega=0.0430$ and $\omega=0.0656$ respectively in the 6-31+(P,D) basis. Our current results: 19.6, 20.7 and 22.5 are within 6% of the previous values and again show little importance of the non-Hellmann-Feynman terms that are neglected in the analytical EOM-CC CI-like expression [48].

Figures 4.3,4.4 and 4.5 show the frequency dependence of the relevant fourth-order processes of *trans*-butadiene in all three basis sets in the 6-31G+(P,D) optimized geometry. The TDHF dispersion is too high (27% in the POL++ basis compared to 17% for EOM at $\omega=0.0430$ a.u. and 90% compared to 64% at $\omega=0.0656$ a.u.), which would also cause an estimated percentage dispersion effect based upon TDHF superimposed on static correlated results to overshoot. That is primarily why the original MBPT(2) estimate of dc-SHG for butadiene was too large at 38.4 [5], or the CCSD result at 34.8 [47]. The alternative estimate of dispersion provided by Bishop's formula [115] based upon EOM-CCSD results for OKE [47] led to a 29.7 value. The formula is

$$\gamma_{\parallel}\left(-\omega_{\sigma};\omega_1,\omega_2,\omega_3\right) = \gamma\left(0\right)\left(1 + A\omega_L^2 + B\omega_L^4 + ...\right),$$
$$\omega_L^2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2 + \omega_3^2. \tag{4.21}$$

For small frequencies we can set $B=0$ and evaluate A in a straightforward manner. For the EOM method, at $\omega=0.0656$ a.u., the A coefficient ranges from 18 to 22 depending on the process and basis set. The TDHF values are on the other hand

scattered widely, especially for multiphoton processes like THG. The TDHF A value for EOKE is 22 but for THG in the POL1++ basis it jumps to 86, making any predictions based on Eq. (4.21) with TDHF completely unreliable. A similar trend can be observed at any frequency studied: at ω=0.0430 a.u. TDHF values of A range from 17 to 29 while EOM is more consistent placing them between 14 and 17. At the 0.0430 a.u. field strength A varies between 14 and 17, that is 18%, while TDHF varies between 17 and 29, giving a 70% error. This means that if we try to use the A coefficient extracted from the TDHF EOKE value (smallest A) and use Bishop's formula to calculate the third harmonic generation (largest value of A), we get an answer with such an error. The 18% error of EOM-CC is also large, but we would expect to reduce it by including the quartic term $B\omega_L^4$. For the higher frequency, ω=0.0656 a.u. the inferior behavior of TDHF is even more evident: while the error in estimating the computed frequencies in the EOM-CCSD is 22%, TDHF variations of 22 to 86 units give 291% error for TDHF. Clearly, TDHF fails to deliver the accuracy expected from a modern *ab initio* method.

To assess two additional important effects; relaxation and triple excitations, we performed a series of finite field differentiations of the dipole moment (Table 4.18). In the 6-31G+(P,D) basis at geometry I orbital relaxation in CCSD decreases the $\gamma(0)$ value by about 7.9% to 18.2. Calculating the CCSD(T) hyperpolarizability with relaxed orbitals gives 19.2, which is 2.1% smaller than the EOM-CCSD un-relaxed figure. For dynamic processes values of these effects only offer estimates. The triples correction was scaled by the percentage dispersion of the EOM-CCSD result to account for frequency dependence, while the orbital relaxation was left constant for all frequencies and geometries.

When the effect of relaxation and triples is included, along with the pure vibrational corrections [118], one gets the POL1++ values for dc-SHG (we exclude

Table 4.18: Adjusted values of dynamic hyperpolarizabilities (dc-SHG) for *trans*-butadiene in the POL1++ basis.

	EOM-CCSD	vibrations[a]	triples[b]	relaxation[c]	total[d]
			geom I		
$\omega = 0.0430$	22.45	-0.50	0.84	-1.55	**21.24**
$\omega = 0.0656$	27.76	-0.40	1.09	-1.55	**26.90**
			geom II		
$\omega = 0.0430$	21.18	-0.50	0.84	-1.55	**19.97**[e]
$\omega = 0.0656$	29.56	-0.40	1.09	-1.55	**28.70**[e]
			geom III		
$\omega = 0.0430$	21.27	-0.50	1.84	-1.55	**20.06**[e]
$\omega = 0.0656$	29.63	-0.40	1.09	-1.55	**28.77**[e]

[a] Kirtman *et al.* [118].

[b] Estimated from the finite derivatives of the dipole moment in the 6-31G+(P,D) basis at geometry I, by the difference between μ for CCSD(T) and CCSD augmented by the EOM-CCSD percentage dispersion correction, 15.1% at 0.043 a.u. and 48.8% at 0.0656 a.u.

[c] Estimated from the finite derivatives of the dipole moment in the 6-31G+(P,D) basis at geometry I, at CCSD.

[d] These should be compared to experimental values: **20.18**± **0.11** at ω=0.0430 a.u. and **27.70**± **1.60** at ω=0.0656 a.u.

[e] It has been pointed out to us by the authors of Ref. 17 that their estimates for the correlated values (using a slightly different geometry), are 21.2 and 29.8 at ω=0.0430 and at ω =0.0656, respectively. These results are in good agreement with ours.

Table 4.19: Excitation energies of *trans*-butadiene at the experimental geometry

Upper row: TDHF values
Lower row: EOM-CC values

mode	6-31G(P,D)	POL1	POL1++	CCSD[a]	CCSDT-3[b]	exp^c
$2A_g$	7.44	7.23	7.07	*7.23*	*6.85*	7.3
	6.93	*7.03*	*6.98*			
$1A_u$	6.85	6.54	6.47	*6.61*	*6.59*	6.66
	6.41	*6.59*	*6.57*			
$1B_g$	6.65	6.21	6.16	*6.40*	*6.37*	6.27
	6.22	*6.30*	*6.27*			
$1B_u$	6.07	5.94	5.92	*6.42*	*6.35*	5.92
	6.62	*6.37*	*6.34*			

[a] In an augmented ANO basis [119]
[b] In an augmented ANO basis [120]
[c] Diarmid [121]

here any zero point vibrational correction) shown in Table 4.18. The excellent agreement of these values with experiment is evident. TDHF hyperpolarizabilities already contain the relaxation effect, while subtracting the pure vibrational contribution will give 16.6, 19.0, 17.8 and 24.2, 28.6 and 27.1 at the three geometries. As an indirect measure of accuracy for hyperpolarizabilities, we can consider some of the low-lying excitation energies provided by different methods. Table 4.19 contains the results: the upper (roman font) row contains uncorrelated TDHF values, the lower, italicized, corresponding to the EOM-CC energies. At the experimental geometry the TDHF seems to offer better agreement with the experiment than EOM-CCSD, especially in the smallest basis set, the 6-31G+(P,D). Even the notoriously difficult Rydberg-valence mixed B_u state [122] has an error of only 0.15 eV, compared to 0.70 eV error on the EOM-CCSD level. Only one CC result obtains less than 6.0 eV [the two-determinant CCSD (TD-CCSD) result is 5.88 eV

[123] at a different geometry], but it is unlikely that TDHF gets this result for the right reason. Watts *et al.* [119] have calculated partial triple excitation contributions to the excitation energies of *trans*-butadiene in an ANO basis set. These are shown in Table 4.19 for the iterative EOM-CCSDT-3 method (J.D. Watts, private communication) to help to assess any significant role for triple excitations. The best results ANO/CCSDT-3 and POL1++/CCSD are quite consistent.

In this chapter we have presented EOM-CCSD correlated, frequency dependent results for four non-linear optical processes and compared those to the corresponding TDHF results. We show dispersion curves up to 0.0882 a.u. Furthermore, we estimate the numerical effects of triple excitations while assuming constant orbital relaxation (this effect would be expected to differ at different frequencies and would vanish at the basis set limit), so we have to avoid claiming too high an accuracy in these calculations. However, the estimates affect the CCSD results by no more than $\pm$ 2 unit, which seems a reasonable error for additional basis set, geometry and correlation effects, too. Hence, at **any** estimated equilibrium geometry, the adjusted EOM-CCSD dc-SHG results average 20.4$\pm$2 at ω=0.0430 a.u. compared to experiment, 20.18$\pm$ 0.11 and 28.1$\pm$2 at ω=0.0656 a.u. compared to 27.70$\pm$ 1.60. The corresponding TDHF results average 17.8 and 26.6 respectively, but are more accurate at the CCSD and experimental geometries.

Although the final averaged values are not too different, the TDHF being somewhat low and the EOM-CC being slightly high, compared to the rather old experimental value, the consistency of the EOM-CC with basis and geometry, and with it offering more consistent A factors in Eq. 4.21, attest to the greater reliability of the correlated result. As a "Pauling point," though, the TDHF results might have some merit for large, linear polyenes.
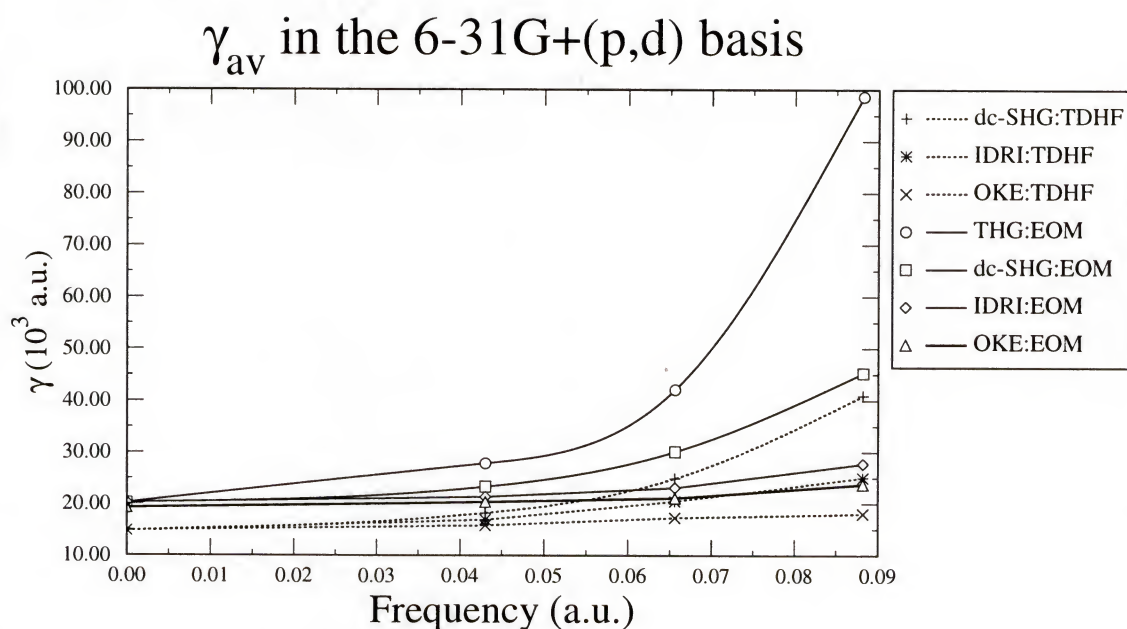
γ_{av} in the 6-31G+(p,d) basis

Figure 4.3: Average dynamic hyperpolarizability of *trans*-butadiene in the 6-31G+(P,D) basis set.
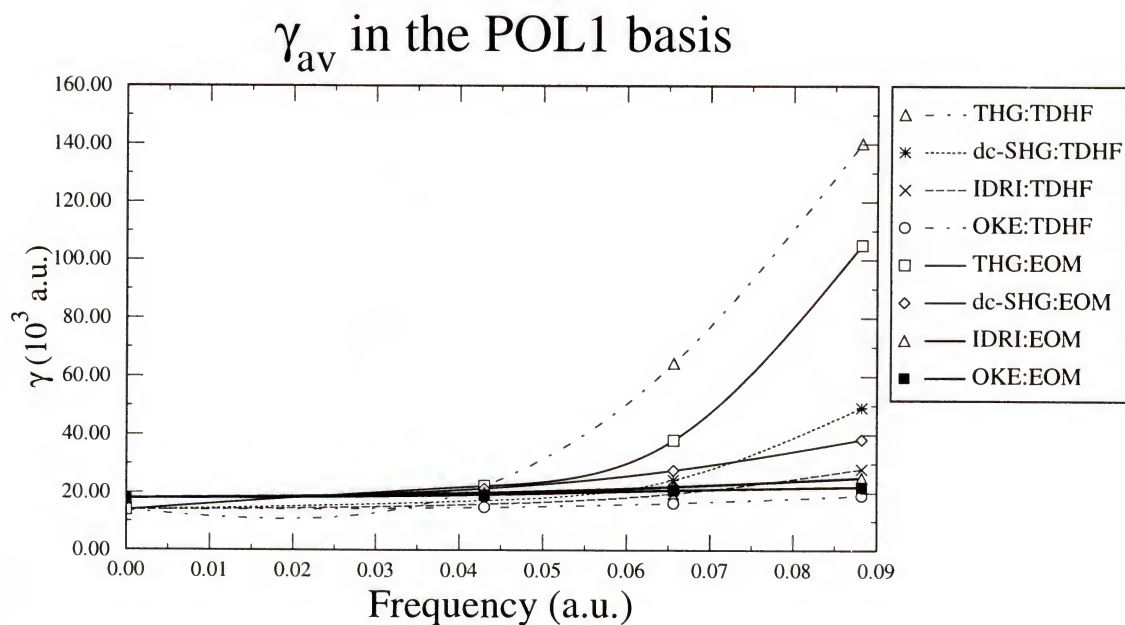
γ_{av} in the POL1 basis

Figure 4.4: Average dynamic hyperpolarizability of *trans*-butadiene in the POL1 basis set.
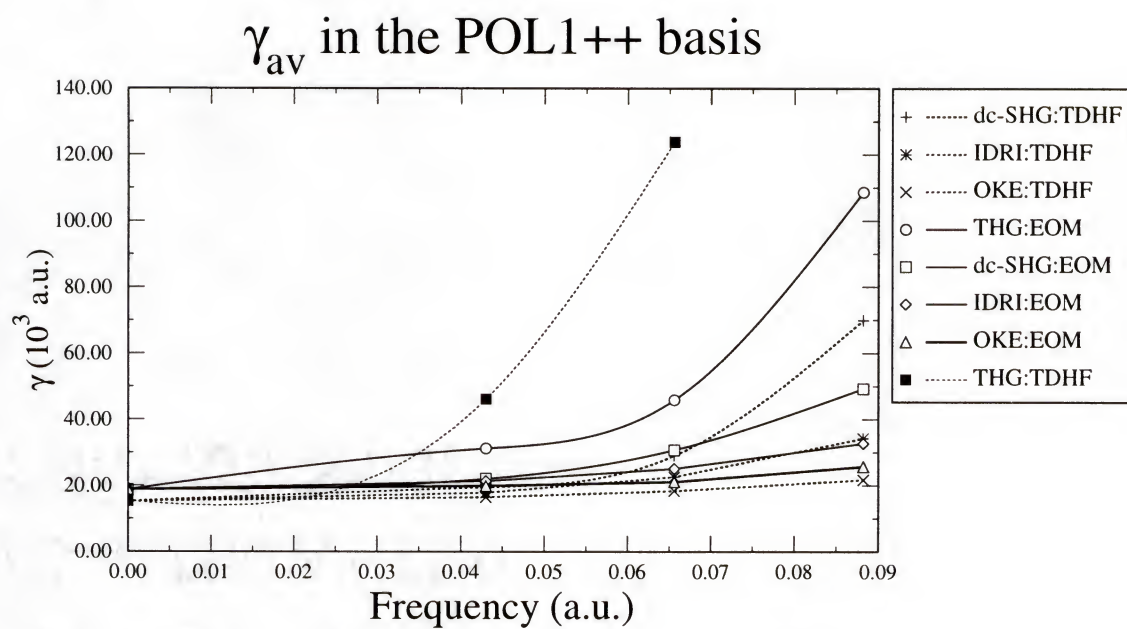
Figure 4.5: Average dynamic hyperpolarizability of *trans*-butadiene in the POL1++ basis set.

CHAPTER 5
CONCLUSIONS AND FUTURE WORK

In this dissertation we derived and applied two new methods for advanced, highly correlated treatment of higher-order electrooptic properties of molecules. Both methods are purely analytical and can be used for both static and dynamic (time dependent) properties. With a set of justified approximations, the resulting formulas are recursive to any order in external perturbation. The first method is based on the Rayleigh-Schrödinger perturbation theory and utilizes the coupled-cluster correlated ground state and resolvent operator working in the space of singly and doubly occupied configurations. We refer to it as RS-EOM-CCSD. The advantages of this method, besides the obvious advantages of the standard EOM-CC methods are: ease of implementation, recursiveness and readiness for application to other than electrooptic processes. The equations for this method derived here are in principle exact and we introduce all the approximations based on their numerical significance and difficulty of implementation.

The current development of quantum chemical methods is diverging in two opposite directions. Applicability and accuracy are very often two mutually exclusive words in quantum chemistry: the more accurate a method is, the larger amount of computational power is needed to tackle a problem limiting potential usefulness of such a method for meaningful chemically interesting applications.

Similarly, the methods presented in this work can be extended in both directions. To achieve results which are closer to the experiment, the next step involves including higher excitations in the coupled cluster wavefunction. Adding approximate triple excitations in the EOM-CC method [95] either as a non-iterative variant [EOM-CCSD(T)] or iterative (EOM-CCSDT-3) proved very advantageous for

improving the overall accuracy of the excitation energies calculations, especially in the case of double excitations. Extension of these algorithms to calculations of the polarizabilities and hyperpolarizabilities is straightforward and is expected to improve the numerical accuracy significantly. Besides decreasing the numerical error, inclusion of approximate triple excitations has been shown [124] to overcome an inherent single-reference burden of the EOM-CC method.

In order to make the presented methods more suitable for tackling real life chemical problems, the RS-EOM-CC and BW-EOM-CC can be easily extended to calculate magneto-optic properties, like Cotton-Mutton effect (hypermagnetizability) [125, 126] or Faraday effect also called circular birefringence. The working equations presented in this thesis need to be extended to include magnetic dipole moment integrals and GIAO orbitals. Linear magnetic properties (NMR shielding and spin-spin coupling constants) have been already implemented by Perera *et al* [127, 128] in the most recent version of the ACESII program package [74] thus making the extension trivial.

As a large portion of the nonlinear optics involves two- or three- dimensional extended systems (polymers, surfaces and crystals) an obvious extension of the proposed method is to include the translational symmetry and boundary conditions. The first correlated and fully analytical way of treating one-dimensional infinite systems has been recently implemented in our group by Sun and Bartlett [129] for the MBPT second-order wavefunction. Both total energies and analytical gradients have been reported and the work on coupled-cluster formalism is on the way.

In order to speed up the calculations of the reduced resolvent, which constitute the major bottleneck in evaluating the recursive EOM-CC equations for (hyper)polarizabilities one can implement the partitioning scheme for the $\bar{H}$ Hamiltonian. Such a technique has been formulated and implemented by Gwaltney *et*

al [69] and Nooijen *et al* [70] for excitation energies and indirect nuclear spin-spin coupling constants respectively.

BW-EOM-CC will also be used to calculate the second- and third-order non-linear optical responses in excited states of molecules. This new and very promising subject has just recently achieved a great deal of attention after experiments showed that the nonresonant hyperpolarizabilities originating from excited states can be by several orders of magnitude larger than those originating from the ground state. Several groups reported both experimental [130] and theoretical [131, 132] results for molecules like diphenylhexatriene, *trans*-octatetraene and smaller polyenes. When pumped with a laser beam at a frequency of electronic resonance, the molecule can maintain a large excited state population for times long enough to perform nonlinear optical measurements. Because this process is nonresonant and involves virtual electronic transitions, one obtains large ultra-fast nonlinear optical responses with minimal background absorption. Detailed theoretical research in this field could help develop new materials with nonlinear susceptibilities many times larger than any material used nowadays.

APPENDIX A:
CANCELLATION OF THE DISCONNECTED TERMS IN THE BW-CCSD METHOD

In the CCSD theory with single and double excitations the T amplitude equations have the form:

$$\langle D_{ij}^{ab}|H - E|\psi_{CCD}\rangle = 0 \Rightarrow$$

$$\langle D_{ij}^{ab}|H|0\rangle + \langle D_{ij}^{ab}|HT_2|o\rangle + \langle D_{ij}^{ab}|H\left(\frac{1}{2}T_2^2\right)|0\rangle = E\langle D_{ij}^{ab}|\psi_{CCD}\rangle$$

$$\langle D_{ij}^{ab}|H|0\rangle + \sum_{k>lc>d}\langle D_{ij}^{ab}|Ht_{kl}^{cd}|D_{kl}^{cd}\rangle + \langle D_{ij}^{ab}|H|X_{QE}\rangle = Et_{ij}^{ab}$$

$$\sum_{k>lc>d}\langle kl||cd\rangle t_{kl}^{cd}t_{ij}^{ab} = E - E_{HF}t_{ij}^{ab}\,, \tag{1}$$

$$(E_0 - E_i)\langle\Phi_i^a|T_1|\Phi_0\rangle \;\; = \;\; \langle\Phi_i^a|\tilde{V}e^{T_1+T_2}|\Phi_0\rangle =$$

$$\langle\Phi_i^a|\tilde{V}\left(1 + T_1 + T_2 + 1/2!T_1^2 + T_1T_2 + 1/3!T_1^3\right)|\Phi_0\rangle\,, \tag{2}$$

$$(E_0 - E_i)\langle\Phi_{ij}^{ab}|T_2|\Phi_0\rangle = \langle\Phi_{ij}^{ab}|\tilde{V}e^{T_1+T_2}|\Phi_0\rangle =$$

$$\langle\Phi_{ij}^{ab}|\tilde{V}\left(1 + T_1 + T_2 + 1/2!T_1^2 + T_1T_2 + 1/3!T_1^3 + T_1T_2 + 1/2!T_1^2 + 1/4!T_1^4\right)|\Phi_0\rangle\,. \tag{3}$$

For the singly excited T amplitudes the above equation can be represented as a sum of the connected and disconnected elements, as we do not work within the linked cluster approximation anymore.

Thus we have

$$(E_0 - E_i)\langle\Phi_i^a|T_1|\Phi_0\rangle = \langle\Phi_i^a|\tilde{V}e^{T_1+T_2}|\Phi_0\rangle_C + \langle\Phi_i^a|\tilde{V}e^{T_1+T_2}|\Phi_0\rangle_{DC} \tag{4}$$

where the disconnected part can be expressed in the form:

$$\langle\Phi_i^a|\tilde{V}e^{T_1+T_2}|\Phi_0\rangle_{DC} = \langle\Phi_i^a|\tilde{V}\left(1/2T_1^2 + T_1T_2 + 1/3!T_1^3\right)|\Phi_0\rangle_{DC} \ . \tag{5}$$

From the above we can infer that

$$\langle\Phi_i^a|\tilde{V}e^{T_1+T_2}|\Phi_0\rangle_{DC} = t_i^a\Delta E_0 \ , \tag{6}$$

with t_i^a being the amplitude coefficients. After substituting the above into Eq. (4) we get

$$(E_0 - E_i)\,t_i^a = \langle\Phi_i^a|\tilde{V}e^{T_1+T_2}|\Phi_0\rangle_C + t_i^a\Delta E_0 \ . \tag{7}$$

Now, when the t amplitudes are completely converged, t_i^a on the left hand side of Eq. (7) and in the righmost term of this equation are the same and we can write

$$(E_0\Delta E - E_i)\,t_i^a = \langle\Phi_i^a|\tilde{V}e^{T_1+T_2}|\Phi_0\rangle_C \ . \tag{8}$$

The above equation contains only connected diagrams and is therefore linked and size consistent. The denominator $(E_0\Delta E - E_i)$ is exactly the BWPT denominator (3.101) containing the exact energy.

Similarily we can prove the size consistency of the doubles equations by expressing the amplitude equations (1) as a sum of connected and disconnected parts:

$$\begin{aligned}
(E_0 - E_i)\,t_{ij}^{ab} &= \langle\Phi_{ij}^{ab}|\tilde{V}e^{T_1+T_2}|\Phi_0\rangle_C + \langle\Phi_{ij}^{ab}|\tilde{V}e^{T_1+T_2}|\Phi_0\rangle_{DC} \\
&\quad - (E_0 - E_i)\left(t_i^at_j^b - t_j^at_i^b\right) \ ,
\end{aligned} \tag{9}$$

where the last term comes from considering

$$-1/2!\,(E_0 - E_i)\,\langle\Phi_{ij}^{ab}|T_1^2|\Phi_0\rangle \tag{10}$$

in the equation for doubly excited amplitudes.

APPENDIX B:
COMPUTATIONAL IMPLEMENTATION

Using an extant linear polarizability code, it is straightforward to modify it in order to calculate hyperpolarizabilities. The only problem lies in evaluation of the perturbation transition matrix between two excited states;

$$\langle \mathbf{h} | \bar{q}_i | \mathbf{h} \rangle = \begin{pmatrix} \langle \mathbf{s} | \bar{q}_i | \mathbf{s} \rangle \langle \mathbf{s} | \bar{q}_i | d \rangle \\ \langle d | \bar{q}_i | s \rangle \langle d | \bar{q}_i | d \rangle \end{pmatrix}.$$

(11)

Above matrix is similar to the $\langle \mathbf{h} | \bar{H} | \mathbf{h} \rangle$ matrix used widely in the EOM theory. Elements of this matrix are evaluated as follows:

$$\langle \mathbf{S} | \hat{q}_k | \mathbf{S} \rangle = t_a^i \bar{M} (ij) - t_a^i \bar{M} (ab),$$

(12)

$$\langle \mathbf{S} | \bar{q}_k | \mathbf{D} \rangle = t_{ij}^{ab} \bar{M} (ai) + t_i^a t_j^b \bar{M} (aj)$$

(13)

$$\langle \mathbf{D} | \bar{q}_k | \mathbf{S} \rangle = t_i^a \bar{M} (ij, kb) - t_i^a \bar{M} (ab, cj),$$

(14)

$$\langle \mathbf{D} | \bar{q}_k | \mathbf{D} \rangle = t_{ij}^{ab} \bar{M} (jk) - t_{ij}^{ab} \bar{M} (bc).$$

(15)

The algorithm is constructed in such a way, that the whole transition matrix is never explicitly evaluated nor stored in the memory or disk. Instead, only one row

of this matrix is being formed, and then it is multiplied by a intermediate vector $\langle \mathbf{h}|X_{k\pm}|0\rangle$ to create one element of the next order intermediate; vector $\langle \mathbf{h}|X_{k\pm}|0\rangle$ to create one element of the next order intermediate;

$$\langle \mathbf{h}|X'_{k\pm}|0\rangle_{ij} = \sum_l \langle \mathbf{h}|\bar{q}_k|\mathbf{h}\rangle_{il} \langle \mathbf{h}|X_{k\pm}|0\rangle_{lj}$$

$$(16)$$

where the intermediate X amplitudes are defined as

$$\langle \mathbf{h}|X_{k\pm}|0\rangle = R_0 \left(\pm\omega\right) * \langle \mathbf{h}|\bar{q}_k|0\rangle.$$

$$(17)$$

The final intermediate, order of which depends on the order of the nonlinear process we want to calculate, is multiplied by the left vector containing lambda:

$$\chi_k^{(n)} = \langle 0| \left(1 + \Lambda\right) \bar{q}|\mathbf{h}\rangle * \langle \mathbf{h}|X_{k\pm}^{(n-1)}|0\rangle$$

$$(18)$$

and the process is repeated for all transition moments.

APPENDIX C:
NAMES, ABBREVIATIONS AND UNITS

Table 1: Names and abbreviations for various linear and nonlinear processes

Property	Process	Abbreviation
$\beta(0; \omega, -\omega)$	Optical Rectification	OR
$\beta(-2\omega; \omega, \omega)$	Second Harmonic Generation	SHG
$\beta(-\omega; \omega, 0)$	dc-Pockels Effect	dc-P
$\gamma(-\omega; \omega, \omega, -\omega)$	Intensity Dependent Refractive Index	IDRI
$\gamma(-\omega_1; \omega_1, \omega_2, -\omega_2)$	ac-Kerr Effect	ac-K
$\gamma(-3\omega; \omega, \omega, \omega)$	Third Harmonic Generation	THG
$\gamma(-\omega; \omega, 0, 0)$	dc-Kerr Effect	dc-K
$\gamma(0, \omega, -\omega, 0)$	dc-Optical Rectification	dc-OR
$\gamma(-2\omega; \omega, \omega, 0)$	dc-Second Harmonic Generation	dc-SHG
$\nu(-\omega; \omega, 0, 0)$	Cotton-Mouton Effect	CME

Table 2: Units and Equivalences

Property	Atomic Unit	SI Equivalent	cgs-esu Equivalent
α	$e^2 a_0^2 E_h^{-1}$	1.6488×10^{-41} $\mathrm{C^2 m^2 J^{-1}}$	2.9635×10^{-25} $\mathrm{Fr^2 cm^2 erg^{-1}}$
β	$e^3 a_0^3 E_h^{-2}$	3.20636×10^{-53} $\mathrm{C^3 m^3 J^{-2}}$	8.63922×10^{-33} $\mathrm{Fr^3 cm^3 erg^{-2}}$
γ	$e^4 a_0^4 E_h^{-3}$	6.23538×10^{-65} $\mathrm{C^4 m^4 J^{-3}}$	5.03670×10^{-40} $\mathrm{Fr^4 cm^4 erg^{-3}}$

REFERENCES

[1] P.A. Franken, A.E. Hill, C.W. Peters, and G. Weinreich. *Phys. Rev. Lett.*, 7:118, 1961.

[2] M. Kaiser and C.G.B. Garrett. *Phys. Rev. Lett.*, 7:229, 1961.

[3] H. Sekino and R.J. Bartlett. *J. Chem. Phys.*, 85:976, 1986.

[4] H. Sekino and R.J. Bartlett. *Int. J. Quantum Chem.*, 43:119–199, 1992.

[5] H. Sekino and R.J. Bartlett. *J. Chem. Phys.*, 94(5):3665, 1991.

[6] P. Jørgensen. *Ann. Rev. Phys. Chem.*, 84:359, 1975.

[7] V. Spirko, Y. Luo, H. Ågren, and P. Jørgensen. *J. Chem. Phys.*, 99:9815–9815, 1993.

[8] D.M. Bishop. *Rev. Mod. Phys.*, 62:343, 1990.

[9] P. Jørgensen and T. Helgaker. *J. Chem. Phys.*, 89:3654, 1988.

[10] Y. Luo, H. Ågren, P. Jørgensen, and K.V. Mikkelsen. *Adv. Quantum Chem.*, 26:165, 1995.

[11] P. Albertsen, P. Jørgensen, and D.L. Yeager. *Mol. Phys.*, 41:409, 1980.

[12] M. Jaszunski, A. Rizzo, and D.L. Yeager. *Chem. Phys. Lett.*, 149:79, 1988.

[13] J.E. Rice and N.C. Handy. *J. Chem. Phys.*, 94:4959, 1991.

[14] J.E. Rice and N. C. Handy. *Int. J. Quantum Chem.*, 43:91, 1992.

[15] K. Sasagane, F. Aiga, and R. Itoh. *J. Chem. Phys.*, 99:3738, 1993.

[16] F. Aiga, K. Sasagane, and R. Itoh. *J. Chem. Phys.*, 99:3779, 1993.

[17] F. Aiga, K. Sasagane, and R. Itoh. *Int. J. Quantum Chem.*, 51:87, 1994.

[18] K. Emrich. *Nucl. Phys.*, A351(1):379, 1981.

[19] D.C. Comeau and R.J. Bartlett. *Chem. Phys. Lett.*, 207(4):414, 1993.

[20] J.F. Stanton and R.J. Bartlett. *J. Chem. Phys.*, 97(4):2299, 1993.

[21] J. F. Stanton and R. J. Bartlett. *J. Chem. Phys.*, 99:5178, 1993.

[22] A.D. Buckingham. *Adv. Chem. Phys.*, 12:107, 1967.

[23] D.A. Kleinman. *Phys. Rev. A*, 126:1977, 1962.

[24] T. Inoue and S. Iwata. *Chem. Phys. Lett.*, 167(6):566, 1990.

[25] T.-S. Nee, R.G. Parr, and R.J. Bartlett. *J. Chem. Phys.*, 64:2216, 1976.

[26] C.E. Dykstra and P.G. Jasien. *Chem. Phys. Lett.*, 109:388, 1984.

[27] D. N. Zubarev. *Soviet Physics Uspekhi*, 3:1870, 1960.

[28] J. Linderberg and Y. Öhrn. *Propagators in Quantum Chemistry*. Academic Press, London and New York, 1973.

[29] P. Jørgensen, H. J. Aa Jensen, and J. Olsen. *J. Chem. Phys.*, 82:3235, 1985.

[30] J. Oddershede, P. Jørgensen, and D. L. Yeager. *Comp. Phys. Rep.*, 2(1):33, 1989.

[31] D.C. Hanna, M.A. Yuratich, and D. Cotter. *Nonlinear Optics of Free Atoms and Molecules*. Springer-Verlag, New York, 1979.

[32] D.M. Bishop. *J. Chem. Phys.*, 100:6536, 1994.

[33] D.J. Thouless. *The Quantum Mechanics of Many-Body Systems*. Academic, New York, 1961.

[34] D. L. Yeager and P. Jørgensen. *Chem. Phys. Lett.*, 65:77, 1979.

[35] E. Dalgaard. *J. Chem. Phys.*, 72:816, 1980.

[36] E.S. Nielsen, P. Jørgensen, and J. Oddershede. *J. Chem. Phys.*, 73:6238, 1980.

[37] H. J. Monkhorst. *Int. J. Quantum Chem. Symp.*, 11:421, 1977.

[38] E. Dalgaard and H.J. Monkhorst. *Phys. Rev. A*, 28:1217, 1983.

[39] H. Koch and P. Jørgensen. *J. Chem. Phys.*, 93:3333, 1990.

[40] C. Hättig, O. Christiansen, H. Koch, and P. Jørgensen. *Chem. Phys. Lett.*, 269:428, 1997.

[41] I. Shavitt and R.J. Bartlett. in preparation.

[42] E. A. Salter, Gary W. Trucks, and Rodney J. Bartlett. *J. Chem. Phys.*, 90:1752, 1989.

[43] R.J. Bartlett. In P. Jørgensen and J. Simons, editors, *Geometrical Derivatives of Energy surfaces and Geometrical Properties*. Reidel, Dordrecht, Holland, 1986.

[44] H. Sekino and R. J. Bartlett. *Chem. Phys. Lett.*, 225:486, 1994.

[45] R.W. Boyd. *Nonlinear Optics.* Academic Press, New York, 1992.

[46] P.B. Rozyczko, P. Piecuch, and R.J. Bartlett. to be published.

[47] H. Sekino and R. J. Bartlett. *Chem. Phys. Lett.*, 234:87, 1995.

[48] P. B. Rozyczko and R. J. Bartlett. *J. Chem. Phys.*, 107:10823, 1997.

[49] L. Brillouin. *J. Phys. Radium*, 3:373, 1932.

[50] E. Wigner. *Math. Naturw. Anz. Ungar. Akad. Wiss.*, 53:477, 1935.

[51] I. Lindgren. *J. Phys. B.*, 7:2441, 1974.

[52] I. Lindgren and J. Morrison. *Atomic Many-Body Theory.* Springer, Berlin, 1982.

[53] P. B. Rozyczko, S. A. Perera, M. Nooijen, and R. J. Bartlett. *J. Chem. Phys.*, 107:6736, 1997.

[54] P.-O. Löwdin. *Phys. Rev. A*, A139:357, 1965.

[55] P.-O. Löwdin. *J. Chem. Phys.*, 43:175, 1965.

[56] P.-O. Löwdin. *Int. J. Quantum Chem.*, 21:69, 1981.

[57] E. Brändas and R.J. Bartlett. *Chem. Phys. Lett.*, 8:153, 1981.

[58] E. Brändas and R.J. Bartlett. *J. Chem. Phys.*, 56:5467, 1972.

[59] I. Hubač and P. Neogràdy. *Phys. Rev. A*, A50:4558, 1994.

[60] P. Čàrsky, V. Hrouda V., Sychrovskỳ, I. Hubač, P. Babinec, P. Mach, J. Urban, and J. Màšik. *Collect. Czech. Chem. Commun.*, 60:1419, 1995.

[61] J. Màšik and I. Hubač. *Collect. Czech. Chem. Commun.*, 62:829, 1997.

[62] P.L. Knight and L. Allen. *Phys. Lett.*, 38A:99, 1972.

[63] J. Oddershede. *Adv. Quantum Chem.*, 11(1):275, 1978.

[64] P. G. Szalay, M. Nooijen, and R. J. Bartlett. *J. Chem. Phys.*, 93:281, 1995.

[65] L. Meissner and R. J. Bartlett. *J. Chem. Phys.*, 92:561, 1990.

[66] R. Kobayashi, H. Koch, and Poul Jørgensen. *Chem. Phys. Lett.*, 219(5):30, 1994.

[67] H. Sekino and R.J. Bartlett. to be published.

[68] J. Geertsen, M. Rittby, and R.J. Bartlett. *Chem. Phys. Lett.*, 164(1):57, 1989.

[69] S. R. Gwaltney, M. Nooijen, and R. J. Bartlett. *Chem. Phys. Lett.*, 248:189, 1996.

[70] S. A. Perera, M. Nooijen, and R. J. Bartlett. *Chem. Phys. Lett.*, 266:456, 1997.

[71] A.J. Sadlej. *Collect. Czech. Chem. Commun.*, 53:1995, 1988.

[72] A.J. Sadlej. *Theor. Chim. Acta*, 79:123, 1991.

[73] H. Sekino and R.J. Bartlett. *Chem. Phys. Lett.*, 234:87, 1995.

[74] Aces II program is a product of the Quantum Theory Project, University of Florida. Authors: J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, , S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balková, D. E. Bernholdt, K. K. Baeck, H. Sekino, P. Rozyczko, C. Huber, R. J. Bartlett. Integral packages included are VMOL (J. Almlöf, J. Olsen P. Taylor); VPROPS (P. R. Taylor); modified version of ABACUS integral derivative package (T. U. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and P. R. Taylor.).

[75] M.A. Spackman. *J. Phys. Chem.*, 93:7594, 1989.

[76] R. D. Amos, N. C. Handy, P. J. Knowles, J. E. Rice, and A. J. Stone. *J. Phys. Chem.*, 89:2186, 1985.

[77] R.J. Bartlett and J.F. Stanton. In K. B. Lipkowitz and D. B. Boyd, editors, *Reviews in Computational Chemistry*, volume 5, pages 65–169. VCH Publishers, Inc., New York, 1994.

[78] H. Sekino and R. J. Bartlett. *J. Chem. Phys.*, 98:3022, 1993.

[79] J. Oddershede and E. N. Svendsen. *Chem. Phys.*, 64:359, 1982.

[80] E.A. Salter, H. Sekino, and R.J. Bartlett. *J. Chem. Phys.*, 87:502, 1987.

[81] E. W. Washburn. *International Critical Tables*. McGraw-Hill, New York, 1982.

[82] G. R. Alms, A. K. Burnham, and W. H. Flygare. *J. Chem. Phys.*, 63:3321, 1975.

[83] N. J. Bridge and A. D. Buckingham. *Proc. Roy. Soc., Ser. A*, A295:334, 1966.

[84] Y. Luo, O. Vahtras, H. Ågren, and P. Jørgensen. *Chem. Phys. Lett.*, 205:555, 1997.

[85] R.J. Bartlett and H. Sekino. In S.P. Karna and A.T. Yates, editors, *Non-Linear Optical Materials: Theory and Modelling*, page 23. American Chemical Society, Boca Raton, 1996.

[86] P. Norman, Y. Luo, D. Jonsson, and H. Ågren. *J. Chem. Phys.*, 106:1827, 1997.

[87] In M.J. Astle R.C. Weast and W.H. Beyer, editors, *Handbook of Chemistry and Physics*, pages E–70. CRC, Boca Raton, 1985.

[88] J. F. Stanton. *Phys. Rev. A*, A49:1698, 1994.

[89] W. Rijks and P. E. S. Wormer. *J. Chem. Phys.*, 88(9):5704, 1988.

[90] W. Rijks and P. E. S. Wormer. *J. Chem. Phys.*, 90(11):6507, 1989.

[91] M. A. Spackman. *J. Chem. Phys.*, 94:1295, 1991.

[92] D. J. Margoliash and W. J. Meath. *J. Chem. Phys.*, 68:1426, 1978.

[93] G. Starkschall and R. G. Gordon. *J. Chem. Phys.*, 54:6635, 1971.

[94] P. W. Fowler, P. Jørgensen, and J. Olsen. *J. Chem. Phys.*, 93:7256, 1990.

[95] J. D. Watts and R. J. Bartlett. *Chem. Phys. Lett.*, 258:581, 1996.

[96] H. Sekino and Rodney J. Bartlett. *J. Chem. Phys.*, 98:3022, 1993.

[97] R. J. Bartlett and G. D. Purvis III. *Phys. Rev. A*, 20:1313, 1979.

[98] H. Sekino and R.J. Bartlett. *J. Chem. Phys.*, 84:2726, 1986.

[99] D.P. Chong and S.R. Langhoff. *J. Chem. Phys.*, 93:570, 1990.

[100] M. Jaszunski, P. Jørgensen, and H.J.Aa. Jensen. *Chem. Phys. Lett.*, 191:293, 1992.

[101] H. Sekino and R. J. Bartlett. *J. Chem. Phys.*, 98:3022, 1993.

[102] D.P. Shelton and J.E. Rice. *Chem. Rev.*, 29:3, 1993.

[103] M.G. Papadopoulos, J. Waite, and A.D. Buckingham. *J. Chem. Phys.*, 102:371, 1995.

[104] J.W. Dudley II and J.F. Ward. *J. Chem. Phys.*, 82:4673, 1985.

[105] D.E. Woon and T.H. Dunning. *J. Chem. Phys.*, 100:2975, 1994.

[106] S. A. Perera, M. Nooijen, and R. J. Bartlett. *J. Chem. Phys.*, 104:3290, 1996.

[107] D.M. Bishop and B. Kirtman. *J. Chem. Phys.*, 95:2646, 1991.

[108] S.M. Cybulski and D.M. Bishop. *J. Chem. Phys.*, 100:2019, 1994.

[109] C. Hättig and B.A. Hess. *Chem. Phys. Lett.*, 233:359, 1995.

[110] T. C. Caves and M. Karplus. *J. Chem. Phys.*, 50:3649, 1969.

[111] R.J.Bartlett. In D. R. Yarkony, editor, *Modern Electronic Structure Theory, part I*, page 1047. CRC, Boca Raton, 1995.

[112] P. Norman, Y. Luo, D. Jonsson, and H. Ågren. *J. Chem. Phys.*, 106:1827, 1997.

[113] G. J. B. Hurst, M. Dupuis, and E. Clementi. *J. Chem. Phys.*, 89:385, 1988.

[114] W. Haugen and M. Traetteberg. *Acta Chem. Scand.*, 20:1726, 1966.

[115] D. M. Bishop. *Chem. Phys. Lett.*, 69:5438, 1978.

[116] D. P. Shelton and J. E. Rice. *Chem. Rev.*, 29:3, 1993.

[117] J. F. Ward and D. S. Elliott. *J. Chem. Phys.*, 69:5438, 1978.

[118] B. Kirtman, J. T. Toto, C. Breneman, C. P. de Melo, and D. M. Bishop. *J. Chem. Phys.*, in press.

[119] J. D. Watts, S. R. Gwaltney, and R. J. Bartlett. *J. Chem. Phys.*, 105:6979, 1996.

[120] J. D. Watts. *Private Communication*.

[121] R. McDiarmid. *J. Chem. Phys.*, 64:514, 1976.

[122] L. Serrano-Andres, M. Merchan, I. Nebot-Gil, R. Lindh, and B. O. Roos. *J. Chem. Phys.*, 98:3151, 1993.

[123] P. G. Szalay and R. J. Bartlett. *J. Chem. Phys.*, 101:4936, 1994.

[124] K. Wilson, P. Piecuch, S. Kucharski, and R.J. Bartlett. *J. Chem. Phys.*, to be published.

[125] C. Rizzo, A. Rizzo, and D.M. Bishop. *Intl. Rev. Phys. Chem.*, 16:81, 1997.

[126] S. Coriani, K. Ruud A. Rizzo, and T. Helgaker. *Chem. Phys.*, 216:53, 1997.

[127] S.A. Perera, H. Sekino, and R.J. Bartlett. *J. Chem. Phys.*, 101:2186, 1994.

[128] S.A. Perera, M. Nooijen, and R.J. Bartlett. *J. Chem. Phys.*, 104:3290, 1996.

[129] J.Q. Sun and R.J. Bartlett. *J. Chem. Phys.*, 107:5058, 1997.

[130] Q.L. Zhou, J.R. Heflin, K.Y. Wong, O. Zamani-Khamiri, and A.F. Garito. *Phys. Rev. A*, 43:1673, 1991.

[131] D.C. Rodenberger, J.R. Heflin, and A.F. Garito. *Phys. Rev. A*, 51:3234, 1995.

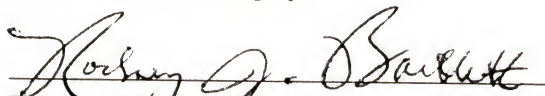[132] D. Jonsson, Y. Luo P. Norman, and H. Ågren. *J. Chem. Phys.*, 105:581, 1996.

BIOGRAPHICAL SKETCH

Piotr Rozyczko was born on December 18, 1968, in a really small city in the southeastern part of Poland. He earned his Technician in Analytical Chemistry diploma in 1988, being 18. Next step in his career was the Master of Science degree in 1993 at the Wroclaw University, where he successfully defended his M.S. thesis on the electronic properties of phosphorus analogs of several nitrogen containing molecules.

In August, 1993, he arrived in Gainesville and begun graduate studies at the University of Florida. His main interest has been advanced quantum chemistry methods, and Quantum Theory Project and especially Dr. Rodney Bartlett's group suited his expectations best.

Assuming that this thesis is turned in on time, he will graduate in December of 1998.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.
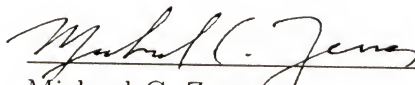
Rodney J. Bartlett, Chairman
Graduate Research Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.
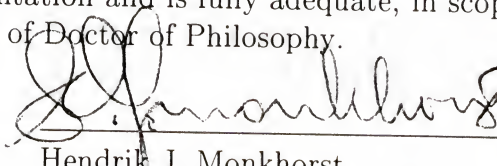
N. Yngve Öhrn
Professor of Chemistry and Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.
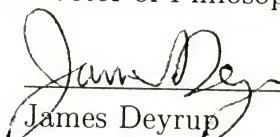
Michael C. Zerner
Professor of Chemistry and Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Hendrik J. Monkhorst
Professor of Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

James Deyrup
Professor of Chemistry

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences, and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1998

_____
Dean, Graduate School